

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

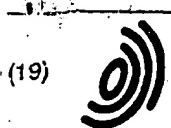
Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 841 406 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
13.05.1998 Bulletin 1998/20

(51) Int. Cl.⁶: **C22C 1/00, B22D 17/00**

(21) Application number: **97119554.0**

(22) Date of filing: **07.11.1997**

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **08.11.1996 JP 296420/96
28.11.1996 JP 317313/96**

(71) Applicant: **UBE INDUSTRIES, LTD.
Ube-shi, Yamaguchi-ken 755 (JP)**

(72) Inventors:
• **Adachi, Mitsuru**
Oaza Kogushi, Ube-shi, Yamaguchi (JP)
• **Sato, Satoru**
Oaza Kogushi, Ube-shi, Yamaguchi (JP)
• **Harada, Yasunori**
Oaza Kogushi, Ube-shi, Yamaguchi (JP)
• **Sasaki, Hiroto**
Oaza Kogushi, Ube-shi, Yamaguchi (JP)

(74) Representative:
Strehl Schübel-Hopf & Partner
Maximilianstrasse 54
80538 München (DE)

(54) **Method of shaping semisolid metals**

(57) In the improved method of shaping a semisolid metal, liquid alloy having crystal nuclei and at a temperature not lower than the liquidus temperature or a partially solid, partially liquid alloy having crystal nuclei and at a temperature less than the liquidus temperature but not lower than the molding temperature is poured into a holding vessel having a thermal conductivity of at least 1 kcal/mh°C, cooled at an average cooling rate of 0.01 °C/s - 3.0 °C/s and held as such until just prior to the start of shaping under pressure, whereby fine primary crystals are generated in said alloy solution and the alloy within said holding vessel is temperature adjusted by induction heating such that the temperatures of various parts of the alloy fall within the desired molding temperature range for the establishment of a specified fraction liquid not later than the start of shaping and the alloy is recovered from said holding vessel, supplied into a forming mold and shaped under pressure. Shaped parts having fine and spherical microstructures can be produced in a convenient, easy and inexpensive manner without relying upon agitation by the conventional mechanical and electromagnetic methods.

EP 0 841 406 A1

Description

Background of the Invention

5 This invention relates to a method of shaping semisolid metals. More particularly, the invention relates to a method of shaping semisolid metals, in which liquid alloy having crystal nuclei and at a temperature not lower than the liquidus temperature or a partially solid, partially liquid alloy having crystal nuclei and at a temperature less than the liquidus temperature but not lower than the molding temperature is poured into a holding vessel, cooled at an average cooling rate in a specified range and held as such until just prior to the start of shaping under pressure, whereby fine primary
10 crystals are generated in the alloy solution and the alloy within said holding vessel is temperature adjusted by induction heating such that the temperatures of various parts of the alloy fall within the desired molding temperature range for the establishment of a specified fraction liquid not later than the start of shaping and the alloy is recovered from the holding vessel, supplied into a forming mold and shaped under pressure.

The invention also relates to a method of shaping semisolid metals, in which a molten aluminum or magnesium
15 alloy containing a crystal grain refiner which is held superheated to less than 50°C above the liquidus temperature is poured directly into a holding vessel without using any cooling jig and held for a period from 30 seconds to 30 minutes as the melt is cooled to the molding temperature where a specified fraction liquid is established such that the temperature of the poured alloy which is either liquid and superheated to less than 10°C above the liquidus temperature or which is partially solid, partially liquid and less than 5°C below the liquidus temperature is allowed to decrease from the initial
20 level and pass through a temperature zone 5°C below the liquidus temperature within 10 minutes, whereby fine primary crystals are generated in the alloy solution, and the alloy is recovered from the holding vessel, supplied into a forming mold and shaped under pressure.

Various methods for shaping semisolid metals are known in the art. A thixo-casting process is drawing researcher's attention these days since it involves fewer molding defects and segregations, produces uniform metallographic structures and features longer mold lives but shorter molding cycles than the existing casting techniques. The billets used in
25 this molding method (A) are characterized by spheroidized structures obtained by either performing mechanical or electromagnetic agitation in temperature ranges that produce semisolid metals or by taking advantage of recrystallization of worked metals. On the other hand, raw materials cast by the existing methods may be molded in a semisolid state. There are three examples of this approach; the first two concern magnesium alloys that will easily produce an equiaxed microstructure and Zr is added to induce the formation of finer crystals [method (B)] or a carbonaceous refiner is added
30 for the same purpose [method (C)]; the third approach concerns aluminum alloys and a master alloy comprising an Al-5% Ti-1% B system is added as a refiner in amounts ranging from 2 - 10 times the conventional amount [method (D)]. The raw materials prepared by these methods are heated to temperature ranges that produce semisolid metals and the resulting primary crystals are spheroidized before molding. It is also known that alloys within a solubility limit are heated
35 fairly rapidly up to a temperature near the solidus line and, thereafter, in order to ensure a uniform temperature profile through the raw material while avoiding local melting, the alloy is slowly heated to an appropriate temperature beyond the solidus line so that the material becomes sufficiently soft to be molded [method (E)]. A method is also known, in which molten aluminum at about 700°C is cast to flow down an inclined cooling plate to form partially molten aluminum, which is collected in a vessel [method (F)].

40 These methods in which billets are molded after they are heated to temperatures that produce semisolid metals are in sharp contrast with a rheo-casting process (G), in which molten metals containing spherical primary crystals are produced continuously and molded as such without being solidified to billets. It is also known to form a rheo-casting slurry by a method in which a metal which is at least partially solid, partially liquid and which is obtained by bringing a molten metal into contact with a chiller and inclined chiller is held in a temperature range that produces a semisolid metal
45 [method (H)].

Further, a casting apparatus (I) is known which produces a partially solidified billet by cooling a metal in a billet case either from the outside of a vessel or with ultrasonic vibrations being applied directly to the interior of the vessel and the billet is taken out of the case and shaped either as such or after reheating with r-f induction heater.

However, the above-described conventional methods have their own problems. Method (A) is cumbersome and the
50 production cost is high irrespective of whether the agitation or recrystallization technique is utilized. When applied to magnesium alloys, method (B) is economically disadvantageous since Zr is an expensive element and speaking of method (C), in order to ensure that carbonaceous refiners will exhibit their function to the fullest extent, the addition of Be as an oxidation control element has to be reduced to a level as low as about 7 ppm but then the alloy is prone to burn by oxidation during the heat treatment just prior to molding and this is inconvenient in operations.

55 In the case of aluminum alloys, about 500 μm is the size that can be achieved by the mere addition of refiners and it is not easy to obtain crystal grains finer than 200 μm . To solve this problem, increased amounts of refiners are added in method (D) but this is industrially difficult to implement because the added refiners are prone to settle on the bottom of the furnace; furthermore, the method is costly. Method (E) is a thixo-casting process which is characterized by heat-

ing the raw material slowly after the temperature has exceeded the solidus line such that the raw material is uniformly heated and spheroidized. In fact, however, an ordinary dendritic microstructure will not transform to a thixotropic structure (in which the primary dendrites have been spheroidized) upon heating. According to method (F), partially molten aluminum having spherical particles in the microstructure can be obtained conveniently but no conditions are available that provide for direct shaping.

What is more, thixo-casting methods (A) - (F) have a common problem in that they are more costly than the existing casting methods because in order to perform molding in the semisolid state, the liquid phase must first be solidified to prepare a billet, which is heated again to a temperature range that produces a semisolid metal. In addition, the billets as the starting material are difficult to recycle and the fraction liquid cannot be increased to a very high level because of handling considerations. In contrast, method (G) which continuously generates and supplies a molten metal containing spherical primary crystals is more advantageous than the thixocasting approach from the viewpoint of cost and energy but, on the other hand, the machine to be installed for producing a metal material consisting of a spherical structure and a liquid phase requires cumbersome procedures to assure effective operative association with the casting machine to yield the final product. Specifically, if the casting machine fails, difficulty arises in the processing of the semisolid metal.

Method (H) which holds the chilled metal for a specified time in a temperature range that produces a semisolid metal has the following problem. Unlike the thixocasting approach which is characterized by solidification into billets, reheating and subsequent shaping, the method (H) involves direct shaping of the semisolid metal obtained by holding in the specified temperature range for a specified time and in order to realize industrial continuous operations, it is necessary that an alloy having a good enough temperature profile to establish a specified fraction liquid suitable for shaping should be formed within a short time. However, the desired rheo-casting semisolid metal which has a fraction liquid and a temperature profile that are suitable for shaping cannot be obtained by merely holding the cooled metal in the specified temperature range for a specified period.

In method (I), a case for cooling the metal in a vessel is employed but the top and the bottom portions of the metal in the vessel will cool faster than the center and it is difficult to produce a partially solidified billet having a uniform temperature profile and immediate shaping will yield a product of nonuniform structure. What is more, considering the need to satisfy the requirement that the partially solidified billet as taken out of the billet case have such a temperature that the initial state of the billet is maintained, it is difficult for the fraction liquid of the partially solidified billet to exceed 50% and the maximum that can be attained practically is no more than about 40%, which makes it necessary to give special considerations in determining injection and other conditions for shaping by diecasting. If the fraction liquid of the billet has dropped below 40%, it could be reheated with a r-f induction heater but is still difficult to attain a fraction liquid in excess of 50% and special considerations must be made in injection and other shaping conditions. In addition, eliminating any significant temperature unevenness that has occurred within the partially solidified billet is a time-consuming practice and it is required, although for only a short time, that the r-f induction heater produce a high power comparable to that required in thixo-casting. In addition it is necessary to install multiple units of the r-f induction heater in order to achieve continuous operation in short cycles.

Another problem with the industrial practice of shaping semisolid metals in a continuous manner is that if a trouble occurs in the casting machine, the semisolid metal may occasionally be held in a specified temperature range for a period longer than the prescribed time. Unless a certain problem occurs in the metallographic structure, it is desired that the semisolid metal be maintained at a specified temperature; in practice, however, particularly in the thixo-casting process where the semisolid metal is held with its temperature elevated from room temperature, the metallographic structure becomes coarse and the billets are considerably deformed (progressively increase in diameter toward the bottom) and, in addition, such billets are usually discarded, which is simply a waste in resources, unless their temperatures are individually controlled.

The present invention has been accomplished under these circumstances of the prior art and its principal object is to provide a method that does not use billets or any cumbersome procedures but which ensures that semisolid metal (including those which have higher values of liquid fraction than what are obtained by the conventional thixo-casting process) which are suitable for subsequent shaping on account of both a uniform structure containing spheroidized primary crystals and uniform temperature profile can be produced in a convenient and easy way with such great rapidity that the power requirement of the r-f induction heater is no more than 50% of what is commonly spent in shaping by the thixo-casting process, said semisolid metals being subsequently shaped under pressure.

Summary of the Invention

The stated object of the invention can be attained by the method of shaping a semisolid metal recited in claim 1, in which liquid alloy having crystal nuclei and being at a temperature not lower than the liquidus temperature or a partially solid, partially liquid alloy having crystal nuclei and being at a temperature less than the liquidus temperature but not lower than the molding temperature is poured into a holding vessel having a thermal conductivity of at least 1

kcal/mh°C, cooled at an average cooling rate of 0.01 °C/s - 3.0 °C/s and held as such until just prior to the start of shaping under pressure, whereby fine primary crystals are generated in said alloy solution and the alloy within said holding vessel is temperature adjusted by induction heating such that the temperatures of various parts of the alloy fall within the desired molding temperature range for the establishment of a specified liquid fraction no later than the start of shaping and the alloy is recovered from said holding vessel, supplied into a forming mold and shaped under pressure.

According to claim 2, the induction heating mentioned in claim 1 is for effecting thermal adjustment such that a specified amount of electric current is applied for a specified time immediately after the pouring of the molten alloy before the representative temperature of the alloy slowly cooling in the holding vessel has dropped to at least 10°C below the desired molding temperature, so that the temperatures of various areas of the alloy within said holding vessel fall within the limits of $\pm 5^\circ\text{C}$ of the desired molding temperature.

According to claim 3, once the temperatures of various parts of the alloy within the holding vessel have been adjusted by induction heating to fall within the desired molding temperature range within a specified time, the temperature of said alloy is held until just before the start of the shaping step by induction heating at a frequency comparable to or higher than the frequency used in the induction heating for the preceding temperature adjustment.

According to claim 4, either the top portion or the bottom portion or both of the holding vessel are heat-retained or heated to a higher temperature than the middle portion or the top and bottom portions of the holding vessel are smaller in wall thickness than the middle portion.

According to claim 5, the alloy within the holding vessel is cooled by blowing either air or water or both against said holding vessel from its outside.

According to claim 6, either air or water or both which are at a specified temperature are blown from at least two different, independently operable heights exterior to the holding vessel such that the blowing conditions and times can be varied freely.

According to claim 7, the alloy to be supplied into the forming mold has a liquid fraction of at least 1.0% but less than 75%.

According to claim 8, the crystal nuclei are generated by vibrating the alloy which builds up in the holding vessel by pouring in a melt superheated to less than 50°C above the liquidus temperature, the vibration being applied to said alloy either by means of vibrating rod which is submerged in the melt during its pouring so that it has direct contact with the alloy or by vibrating not only the vibrating rod but also the holding vessel as the alloy is poured into said holding vessel.

According to claim 9, the crystal nuclei are generated by pouring a molten aluminum alloy into the holding vessel, said alloy being held superheated to less than 50°C above the liquidus temperature and containing 0.001% - 0.01% B and 0.005% - 0.3% Ti.

According to claim 10, the crystal nuclei are generated by pouring a molten magnesium alloy into the holding vessel, said alloy being held superheated to less than 50°C above the liquidus temperature and containing 0.01% - 1.5% Si and 0.005% - 0.1% Sr or 0.05% - 0.30% Ca alone.

The stated of the invention can also be attained by the method of shaping a semisolid metal recited in claim 11, in which a molten aluminum or magnesium alloy containing a crystal grain refiner which is held superheated to less than 50°C above the liquidus temperature is poured directly into a holding vessel without using any cooling jig and held for a period from 30 seconds to 30 minutes as the melt is cooled to the molding temperature where a specified liquid fraction is established such that the temperature of the poured alloy which is liquid and superheated to less than 10°C above the liquidus temperature or which is partially solid, partially liquid and less than 5°C below the liquidus temperature is allowed to decrease from the initial level and pass through a temperature zone 5°C below the liquidus temperature within 10 minutes, whereby fine primary crystals are generated in said alloy solution, and the alloy is recovered from the holding vessel, supplied into a forming mold and shaped under pressure.

According to claim 12, the aluminum alloy mentioned in claim 11 has 0.03% - 0.30% Ti added and superheated to less than 30°C above the liquidus temperature as it is poured into the holding vessel.

According to claim 13, the aluminum alloy mentioned in claim 11 has 0.005% - 0.30% Ti and 0.001% - 0.01% B added and superheated to less than 50°C above the liquidus temperature as it is poured into the holding vessel.

According to claim 14, the temperature of the alloy poured into the holding vessel is held by temperature adjustment through induction heating such that the temperatures of various parts of said alloy within said holding vessel are allowed to fall within the desired molding temperature range for the establishment of a specified fraction liquid not later than the start of shaping.

Brief Description of the Invention

Fig. 1 is a diagram showing a process sequence for the semisolid forming of a hypoeutectic aluminum alloy having a composition at or above a maximum solubility limit according to the invention;

Fig. 2 is a diagram showing a process sequence for the semisolid forming of a magnesium or aluminum alloy having a composition within a maximum solubility limit according to the invention;

Fig. 3 shows the process flow in Examples 1 - 10 which starts with the generation of spherical primary crystals and ending with the molding step;

Fig. 4 shows diagrammatically the metallographic structures obtained in the respective steps shown in Fig. 3;

Fig. 5 is an equilibrium phase diagram for an Al-Si alloy as a typical aluminum alloy system according to the invention;

Fig. 6 is an equilibrium phase diagram for a Mg-Al alloy as a typical magnesium alloy system according to the invention;

Fig. 7 is a diagrammatic representation of a micrograph showing the metallographic structure of a shaped part (of AC4CH alloy) according to an example of the invention;

Fig. 8 is a diagrammatic representation of a micrograph showing the metallographic structure of a shaped part (of AC4CH alloy) according to a comparative examples;

Fig. 9 is a graph illustrating the correlation between the temperature distribution of AC4CH alloy in a holding vessel and its cooling rate according to an example of the invention;

Fig. 10 is a graph showing the effect of r-f induction heating on the temperature distribution of AC4CH alloy in a holding vessel according to an example of the invention;

Fig. 11 is a graph showing the effect of r-f induction heating on the temperature distribution of AC4CH alloy in a holding vessel according to another example of the invention;

Fig. 12 illustrates how holding by r-f induction heating affects the compositional homogenization of a semisolid metal after the molding temperature was reached in an example of the invention;

Fig. 13 shows a process flow in the invention which starts with the generation of spherical primary crystals and which ends with the molding step;

Fig. 14 is a graph showing how the B content and the degree of superheating of a melt during pouring affect the size and morphology of the primary crystals of AC4CH alloy (Al-7% Si-0.3% Mg-0.15% Ti) according to the invention;

Fig. 15 is a graph showing how the B content and the degree of superheating of a melt during pouring affect the size and morphology of the primary crystals of 7075 alloy (Al-5.5% Zn-2.5% Mg-1.6% Cu-0.15% Ti) according to the invention;

Fig. 16 is a diagrammatic representation of a micrograph showing the metallographic structure of a shaped part (from AC4CH-0.15% Ti) according to an example of the invention;

Fig. 17 is a diagrammatic representation of a micrograph showing the metallographic structure of a shaped part (from AZ91-0.01% Sr-0.4% Si) according to another example of the invention;

Fig. 18 is a diagrammatic representation of a micrograph showing the metallographic structure of a shaped part (from 7075-0.15% Ti-0.002% B) according to yet another example of the invention;

Fig. 19 is a diagrammatic representation of a micrograph showing the metallographic structure of a shaped part (from AC4CH-0.15% Ti) according to a comparative example;

Fig. 20 is a diagrammatic representation of a micrograph showing the metallographic structure of a shaped part (from AZ91) according to another comparative example;

Fig. 21 is a diagrammatic representation of a micrograph showing the metallographic structure of a shaped part (from AZ91-0.01% Sr) according to yet another comparative example; and

Fig. 22 is a diagrammatic representation of a micrograph showing the metallographic structure of a shaped part (from 7075) according to still another comparative example.

Detailed Description of the Invention

In the present invention, liquid alloy having crystal nuclei and at a temperature not lower than the liquidus temperature or a partially solid, partially liquid alloy having crystal nuclei and at a temperature less than the liquidus temperature but not lower than the molding temperature is poured into a holding vessel having a thermal conductivity of at least 1 kcal/mh°C, is cooled at an average cooling rate of 0.01 °C/s - 3.0 °C/s and held as such until just prior to the start of shaping under pressure, whereby fine primary crystals are generated in said alloy solution and the alloy within said holding vessel is temperature adjusted by induction heating such that the temperatures of various parts of the alloy fall within the desired molding temperature range for the establishment of a specified fraction liquid not later than the start of shaping and the alloy is recovered from said holding vessel, supplied into a forming mold and shaped under pressure. Since the temperature control of the alloy prior to the shaping step is performed in the ideal manner, satisfactory shaped parts can be obtained that have a homogeneous structure containing spheroidized primary crystals.

It is also within the scope of the invention that a molten aluminum containing Ti either alone or in combination with B or a molten magnesium alloy containing Ca or both Si and Sr, is held superheated to less than 50°C above the liquidus temperature, poured directly into a holding vessel without using any cooling jig and held for a period from 30 seconds to 30 minutes as the melt is cooled to the molding temperature where a specified fraction liquid is established such

that the temperature of the poured alloy which is liquid and superheated to less than 10°C above liquidus temperature or which is partially solid, partially liquid and less than 5°C below the liquidus temperature is allowed to decrease from the initial level and pass through a temperature zone 5°C below the liquidus temperature within 10 minutes, whereby fine primary crystals are generated in said alloy solution and the temperatures of various parts of the alloy within said holding vessel are adjusted such that by means of induction heating and local heating or heat retention of the vessel, said temperatures will fall within the desired molding temperature range for the establishment of a specified fraction liquid not later than the start of shaping, and said alloy is recovered from said holding vessel, supplied into a forming mold and shaped under pressure. As a result, satisfactory shaped parts are obtained that have a fine and uniform microstructure.

Examples

Examples of the invention will now be described in detail with reference to accompanying drawings Figs. 1-12, in which: Fig. 1 is a diagram showing a process sequence for the semisolid forming of a hypoeutectic aluminum alloy having a composition at or above a maximum solubility limit; Fig. 2 is a diagram showing a process sequence for the semisolid forming of a magnesium or aluminum alloy having a composition within a maximum solubility limit; Fig. 3 shows a process flow starting with the generation of spherical primary crystals and ending with the molding step; Fig. 4 shows diagrammatically the metallographic structures obtained in the respective steps shown in Fig. 3; Fig. 5 is an equilibrium phase diagram for an Al-Si alloy as a typical aluminum alloy system; Fig. 6 is an equilibrium phase diagram for a Mg-Al alloy as a typical magnesium alloy system; Fig. 7 is a diagrammatic representation of a micrograph showing the metallographic structure of a shaped part according to the invention; Fig. 8 is a diagrammatic representation of a micrograph showing the metallographic structure of a shaped part according to the prior art; Fig. 9 is a graph illustrating the correlation between the temperature distribution of AC4CH alloy in a holding vessel and its cooling rate; Fig. 10 is a graph showing the effect of r-f induction heating on the temperature distribution of AC4CH alloy in a holding vessel; Fig. 11 is another graph showing the effect of r-f induction heating on the temperature distribution of AC4CH alloy in a holding vessel; and Fig. 12 illustrates how holding by r-f induction heating affects the compositional homogenization of a semisolid metal after the molding temperature was reached.

Fig. 13 - 18 relate to Examples 11 - 14 of the invention. Fig. 13 shows a process flow starting with the generation of spherical primary crystals and ending with the molding step; Fig. 14 is a graph showing how the B content and the degree of superheating of a melt during pouring affect the size and morphology of the primary crystals of AC4CH alloy (Al-7% Si-0.3% Mg-0.15% Ti); Fig. 15 is a graph showing how the B content and the degree of superheating of a melt during pouring affect the size and morphology of the primary crystals of 7075 alloy (Al-5.5% Zn-2.5% Mg-1.6% Cu-0.15% Ti); and Fig. 16 - 18 are diagrammatic representation of a micrographs showing the metallographic structures of shaped parts within the scope of the invention.

Fig. 19 - 22 are diagrammatic representation of a micrographs showing the metallographic structures of a shaped parts.

As shown in Figs. 1, 2, 3, 5 and 6, the first step of the process according to the invention comprises superheating the melt of a hypoeutectic aluminum alloy of a composition at or above a maximum solubility or a magnesium or aluminum alloy of a composition within a maximum solubility limit, holding the melt superheated to less than 5°C above the liquidus temperature as it is poured into a holding vessel, with a vibrating rod being submerged within the melt in the holding vessel and vibrated in direct contact with the melt so as to vibrate the latter and, after the end of the pouring, immediately pulling up said vibrating rod so that it disengages from the melt.

Thus, there is obtained the liquid alloy having crystal nuclei and at a temperature not lower than the liquidus temperature or the partially solid, partially liquid alloy having crystal nuclei and at a temperature less than the liquidus temperature but not lower than the holding temperature. Subsequently, either alloy in said holding vessel is cooled to the molding temperature, where a specified fraction liquid is established, at an average cooling rate of 0.01 - 3.0 °C/s with a cooling medium such as air at room temperature being blown against said holding vessel from the outside and the alloy is held as such until just prior to the start of shaping under pressure, whereby fine primary crystals are generated in said alloy solution and the alloy within said holding vessel is temperature adjusted by induction heating such that the temperatures of various parts of the alloy fall within the desired molding temperature range for establishment of a specified fraction liquid not later than the start of shaping and said alloy is recovered from said holding vessel, supplied into a forming mold and shaped under pressure.

Another process according to the invention is also shown in Fig. 13 and the first step comprises superheating the melt of a hypoeutectic aluminum alloy of a composition at or above a maximum solubility or a magnesium or aluminum alloy of a composition within a maximum solubility limit, both alloys containing a crystal grain refiner (which is hereunder referred to as "refiner"), holding the melt superheated to less than 50°C above the liquidus temperature as it is poured into a holding vessel. Then, the alloy is held for a period from 30 seconds to 30 minutes as the melt is cooled to the molding temperature whereas specified fraction liquid is established such that the temperature of either the poured liq-

liquid alloy superheated to less than 10°C above the liquidus temperature or the poured partially solid, partially liquid alloy which is less than 5°C below the liquidus temperature is allowed to decrease from the initial level and pass through a temperature range 5°C below the liquidus temperature within 10 minutes, whereby fine primary crystals are generated in said alloy solution, and the alloy is recovered from the holding vessel 30, supplied into a forming mold 60 and shaped under pressure.

In practice, a molten alloy which has been poured into the holding vessel is cooled by blowing air or water from the outside of the vessel until the melt reaches the predetermined temperature which is set above the temperature of shaping, while the temperature of the upper and the lower portions of the vessel is being maintained constant. Further, the temperature of various portions of the melt in the holding vessel is adjusted by induction heating so that the melt may have a temperature within the desired molding temperature range to establish a specified fraction of liquid before the start of shaping at latest.

The term "a specified liquid fraction" means a relative proportion of the liquid phase which is suitable for pressure forming. In high-pressure casting operations such as die casting and squeeze casting, the liquid fraction is less than 75%, preferably in the range of 40% - 65%. If the liquid fraction is less than 40%, not only is it difficult to recover the alloy from the holding vessel 30 but also the formability of the raw material is poor. If the liquid fraction exceeds 75%, the raw material is so soft that it is not only difficult to handle but also less likely to produce a homogeneous microstructure because the molten metal will entrap the surrounding air when it is inserted into the sleeve for injection into a mold on a die-casting machine or segregation develops in the metallographic structure of the casting. For these reasons, the liquid fraction for high-pressure casting operations should not be more than 75%, preferably not more than 65%.

In extruding and forging operations, the liquid fraction ranges from 1.0% to 70%, preferably from 10% to 65%. Beyond 70%, an uneven structure can potentially occur. Therefore, the liquid fraction should not be higher than 70%, preferably 65% or less. Below 1.0%, the resistance to deformation is unduly high; therefore, the liquid fraction should be at least 1.0%. If extruding or forging operations are to be performed with an alloy having a liquid fraction of less than 40%, the alloy is first adjusted to a liquid fraction of 40% and more before it is taken out of the holding vessel and thereafter the liquid fraction is lowered to less than 40%.

The "holding vessel" as used in the invention is metallic nonmetallic vessel (including a ceramic vessel), or a metallic vessel having a surface coated with nonmetallic materials, or a metallic vessel composited with nonmetallic materials. Coating the surface of a metallic vessel with nonmetallic materials is effective in preventing the sticking of the metal. The holding vessel may be heated either internally or externally by means of a heater; alternatively, a r-f induction heater may be employed.

The term "the representative temperature" as used herein refers to the center temperature of the alloy charged into holding vessel. More specifically, it means the temperature at the center of the alloy in the holding vessel in both the height and radial directions. In practical operations, however, it is difficult to measure the temperature of the alloy center in both directions and, instead, the temperature in a position a specified depth (say, 1 cm) below the surface of a semi-solid metal is measured. From this temperature, the representative temperature is estimated on the basis of the preliminarily established relationship between the representative temperature and the temperatures of various parts of the alloy.

According to the invention, two methods are proposed for generating crystal nuclei, first by using vibrating jig during the pouring of a melt into the vessel, and second by using a low-temperature melt containing a refiner. Known methods may of course be employed to generate crystal nuclei, and they include the "seed pouring" method utilizing crystal liberation (the melt is cast to flow on a water-cooled inlined cooling plate) and mixing two liquid phases having different melting points. According to the invention, the crystal nuclei are generated "by vibrating the alloy which builds up in the holding vessel by pouring in a melt, the vibration being applied to said alloy by means of a vibrating rod which is submerged in the melt during its pouring so that it has direct contact with the alloy". This does not mean that the melt is poured on to the vibrating rod placed in the holding vessel; rather, the liquid alloy which is building up in the holding vessel after it was poured in is vibrated by means of the vibrating rod submerged in said alloy (when the pouring ends, the vibrating rod is immediately disengaged from the melt).

The term "vibration" as used herein is in no way limited in terms of the type of the vibrator used and the vibrating conditions (frequency and amplitude) and any commercial pneumatic and electric vibrators may be employed. As for the applicable vibrating conditions, the frequency typically ranges from 10 Hz to 50 kHz, preferably from 50 Hz to 1 kHz, and the amplitude ranges from 1 mm to 0.1 μ m, preferably from 500 μ m to 10 μ m, per side.

The method of pouring the refiner-containing low-temperature melt into the holding vessel 30 should be such that crystal nuclei (fine crystals) can be generated in the poured melt. In order to ensure that the refiner which works as a foreign nucleus or as an element to accelerate the liberation of crystals will manifest its effect, the melt must be poured in at a specified rate and, in addition, it must be superheated to a temperature that is above the liquidus temperature by a specified degree. The degree of superheating varies with the kind of the refiner to be added and the amount of its addition (the criticality of the degree of superheating will be described later in this specification).

If the melt is poured in too fast, it is prone to entrap the surrounding air; on the other hand, if the melt is poured in

too slowly, the intended effect of adding the refiner is not achieved and it is not efficient from an engineering viewpoint. Therefore, it is important that the metal be poured in at an appropriate rate within the range that does not cause entrapping of the surrounding air. The appropriate rate is faster than what is determined by equation (1) but slower than the rate determined by equation (2):

$$Y = 0.015X + 0.02 \text{ (preferably } Y = 0.03X + 0.02) \quad \text{Eq. (1)}$$

$$Y = 0.017X + 0.06 \quad \text{Eq. (2)}$$

where Y is the pouring rate (kg/s) and X is the weight of the melt (kg).

Titanium (Ti) may be added to the aluminum alloy as a refiner either alone or in combination with boron (B) in order to produce fine spherical crystal grains. If Ti is to be added alone, its refining effect is small if the addition is less than 0.03%. Beyond 0.30%, coarse Ti compounds well develop to reduce the ductility. Hence, Ti is added in an amount of 0.03% - 0.30%.

If both Ti and B are to be added, the effect of Ti is small if its addition is less than 0.005%. Beyond 0.30%, coarse Ti compounds will develop to reduce the ductility. Hence, Ti is added in an amount of 0.005% - 0.30% in combination with B. Boron (B), when added in combination with Ti, promotes the refining process. However, if its addition is less than 0.001%, only a small refining effect occurs. The effect of B is saturated if it is added in excess of 0.01%. Therefore, the addition of B should range from 0.001% to 0.01%.

Calcium (Ca) or the combination of Sr and Si may be added to the magnesium alloy as a refiner. If Ca is to be added, its refining effect is small if the addition is less than 0.05%. Beyond 0.30%, the effect of Ca is saturated. Therefore, the addition of Ca should range from 0.05% to 0.30%. In the case of combined addition of Sr and Si, only a small refining effect occurs if Sr is added in an amount of less than 0.005%. The effect of Sr is saturated if it is added in excess of 0.1%. Therefore, the addition of Sr should range from 0.005% to 0.1%. Silicon (Si), when added in combination with Sr, promotes the refining process. However, if its addition is less than 0.01%, only a small refining effect occurs. If Si is added in excess of 1.5%, its effect is saturated and, what is more, there occurs a drop in ductility. Therefore, the addition of Si should range from 0.01% to 1.5%.

According to the invention, semisolid metal forming will proceed by the following specific procedure. In step (1) of the process shown in Figs. 3 and 4, a complete liquid form of metal M1 is contained in a ladle 10. In step (2), the alloy M1 is poured into a holding vessel 30 (which is either a ceramic or a ceramic-coated metallic vessel) as a vibrating rod 20 submerged in the alloy to have direct contact with it is vibrated to impart vibrations to the alloy, with the holding vessel 30 being vibrated with a vibrator 40 as required during the pouring of the melt. After the end of the pouring operation, the vibrating rod 20 is immediately pulled up so that crystal nuclei are generated in the alloy which is either liquid or partially liquid at a temperature near the liquidus temperature.

In subsequent step (3), the alloy is cooled at an average cooling rate of 0.01 °C/s - 3.0 °C/s and held as such within the holding vessel 30 until just prior to the start of shaping under pressure so that fine primary crystals are generated in said alloy solution; at the same time, induction heating (i.e., energization of a heating coil 80 around the holding vessel 30) is performed to effect temperature adjustment right after the pouring of the melt such that the temperatures of various parts of the alloy in the vessel will fall within the desired molding temperature range for establishment of a specified fraction liquid not later than the start of the molding step. For cooling the alloy, air (or water) 90 is blown against the holding vessel from its outside. If necessary, both the tip and bottom portions of the holding vessel 30 may be heat-retained with a heat insulator or heated so that the alloy is held partially molten to generate fine spherical (non-dendritic) primary crystals from the introduced crystal nuclei. Metal M2 thus obtained at a specified fraction liquid is inserted from the inverted holding vessel 30 [see step (3)-d] into a die casting injection sleeve 50 and thereafter pressure formed within an mold cavity 60a on a die casting machine to produce a shaped part [step (4)].

In the other method of the invention, semisolid metal forming will proceed by the following specific procedure. In step (1) of the process shown in Figs. 3 and 4, a complete liquid form of metal M1 containing a refiner is charged into a pouring ladle 10 (which is hereunder sometimes referred to simply as "ladle"). In step (2), the melt is gently but rapidly poured into a holding vessel 30 (which is either a ceramic coated or a ceramic vessel), thereby forming either a liquid or a partially solid, partially liquid alloy that contain crystal nuclei (fine crystal grains) and which are at a temperature near the liquidus temperature.

Subsequently in step (3), the temperature of the poured alloy which is either liquid and superheated to less than 10°C above the liquidus temperature of which is partially solid, partially liquid and less than 5°C below the liquidus temperature is allowed to decrease from the initial level and pass through a temperature zone 5°C below the liquidus temperature within 10 minutes, whereby fine primary crystals are generated in said alloy solution; at the same time, induction heating (i.e., energization of a heating coil 80 around the holding vessel 30) is performed to effect temperature adjustment such that the temperatures of various parts of the alloy in the vessel 30 will fall within the desired molding temperature range for the establishment of a specified fraction liquid not later than the start of the molding step.

Fig. 9 is a graph illustrating the correlation between the temperature distribution of AC4CH alloy in the holding vessel and its cooling rate. In other words, Fig. 9 shows the effect of cooling rate (for cooling from 615°C to 585°C) on the temperature distribution of AC4CH alloy in the holding vessel 30; obviously, the temperature distribution becomes wider as the cooling rate increases.

Fig. 9a shows the case where the cooling rate was 0.3 °C/s; in this case, the alloy was cooled with air being blown from the outside of the holding vessel, the top portion of which was heat-retained with a heat insulator which was also provided on the underside of the vessel. Fig. 9b shows the case where the cooling rate was 0.2 °C/s; in this case, both the top and bottom portions of the vessel were heat-retained with a heat insulator and the alloy was cooled in the atmosphere.

Fig. 10 is a graph showing the effect of r-f induction heating on the temperature distribution of AC4CH alloy in the holding vessel. According to the invention when the representative temperature of the alloy (its center temperature as it is in the holding vessel) has reached +3°C above the desired molding temperature the blowing of air is stopped and r-f induction heating is started when the desired temperature is reached.

Fig. 11 is another graph showing the effect of r-f induction heating on the temperature distribution of AC4CH alloy in the holding vessel. According to the invention, when the representative temperature of the alloy (its center temperature as it is within the holding vessel) has reached a temperature 11°C below the desired molding temperature, the blowing of air is stopped and r-f induction heating is started.

If the r-f induction heater is started to operate before the temperature becomes unduly lower than the desired molding temperature, the temperatures of various parts of the alloy in the holding vessel 30 can be maintained at the desired molding temperature in a short time with small electric power. On the other hand, if the r-f induction heater becomes operational after the alloy's temperature has become at least 10°C lower than the desired molding temperature, it is not easy to maintain various parts of the alloy in the vessel at uniform temperature without performing induction heating with high electric power for a prolonged time. Therefore, the induction heating should comprise at least one application of electric current in a specified amount for specified period of time before the representative temperature of the alloy slowly cooling in the holding vessel 30 has dropped to at least 10°C below the desired molding temperature.

Fig. 12 illustrates how holding by r-f induction heating affects the compositional homogenization of a semisolid metal after the molding temperature has been reached. Each of the diagrams in Fig. 12 is a vertical section of the alloy in the holding vessel 30; Fig. 12a shows the state of the alloy which has attained the molding temperature; Fig. 12b shows the state of the alloy which was held for 20 minutes by heating with the r-f induction heater at a frequency of 8 kHz; and 12c shows the state of the alloy which was held for 20 minutes by heating with the r-f induction heater at a frequency of 40 kHz.

The operating frequency of the r-f induction heater is 8 kHz before the alloy's temperature is adjusted to the molding temperature. A peculiar phenomenon which does not occur at the time the molding temperature has been reached (Fig. 12a) is observed if the alloy is held for a prolonged time; that is the uneven occurrence of the liquid phase in the top peripheral portion of the semisolid metal which is inherently a uniform mixture of the liquid and solid phases (the concentrated liquid phase is shown shaded in Fig. 12b).

This problem may be explained as follows: the metal in the holding vessel 30 forms "mushrooms" during the induction heating and the liquid phase of the semisolid metal floats in the top portion of the vessel mainly due to the agitating force. To suppress this agitating force, induction heating is performed at a higher frequency after the semisolid metal in the holding vessel has been adjusted to the molding temperature; consequently, the degree of the uneven occurrence of the liquid phase can be reduced. To this end, after the temperatures of the various parts of the alloy in the holding vessel have been adjusted by induction heating to fall within the desired molding temperature range within a specified time, the same alloy is held within the stated range until just prior to the start of the molding step by continuing the induction heating at a frequency either comparable to or higher than the frequency used in the preceding induction heating.

The semisolid metal forming process of the invention shown in Figs. 1, 2, 3, 4 and 11 has the following differences from the conventional thixocasting and rheocasting methods. In the invention method, the dendritic primary crystals that have been generated within a temperature range of from the semisolid state are not ground into spherical grains by mechanical or electromagnetic agitation as in the prior art but the large number of primary crystals that have been generated and grown from the introduced crystal nuclei with the decreasing temperature in the range for the semisolid state are spheroidized continuously by the heat of the alloy itself (which may optionally be supplied with external heat and held at a desired temperature). In addition, the semisolid metal forming method of the invention is characterized by the production of a uniform microstructure and temperature distribution by r-f induction heating with lower output and it is a very convenient and economical process since it does not involve the step of partially melting billets by reheating in the thixo-casting process.

The nucleating, spheroidizing and molding conditions that are respectively set for the steps shown in Fig. 3, namely, the step of pouring the metal into the holding vessel 30, the step of generating and spheroidizing primary crystals and the forming step, are set forth below more specifically. Also discussed below is the criticality of the numerical limitations the invention should have.

If crystal nuclei are to be generated by (1) applying vibrations to the melt in the holding vessel 30 or (2) pouring a Ti- and B-containing aluminum alloy or a Si and Sr-containing magnesium alloy or a Ca-containing magnesium alloy directly into the holding vessel, the melt should be superheated to less than 50°C, preferably less than 30°C, above the liquidus temperature. If crystal nuclei are to be generated by pouring a Ti-containing aluminum alloy into the holding vessel, the melt should be superheated to less than 30°C above the liquidus temperature. If the temperature of the melt being poured into the holding vessel is higher than these limits, the following phenomena will occur; (1) only a few crystal nuclei are generated; (2) the temperature of the alloy as poured into the vessel is higher than the liquidus temperature and, hence, the number of residual crystal nuclei is small and the size of primary crystals is large enough to produce amorphous dendrites.

If the upper or lower portion of the holding vessel 30 is not heated or heat-retained while the alloy M1 poured into the vessel is cooled to establish a fraction liquid suitable for molding, dendritic primary crystals are generated in the skin of the alloy M1 in the top and/or bottom portion of the vessel or a solidified layer will grow to cause nonuniformity in the temperature distribution of the metal in the holding vessel 30; as a result, even if r-f induction heating is performed, the alloy having the specified fraction liquid cannot be discharged from the inverted vessel 30 or the remaining solidified layer within the holding vessel 30 either introduces difficulty into the practice of continued shaping operation or prevents the temperature distribution of the alloy from being improved in the desired way.

In order to avoid these problems, if the poured metal is held in the vessel for a comparatively short time until the molding temperature is reached, the top and/or bottom portion of the holding vessel is heated or heat-retained at a higher temperature than the middle portion in the cooling process; if necessary, both the top and bottom portions of the holding vessel 30 may be heated not only in the cooling process but also before the pouring step.

If the wall thickness of the holding vessel 30 is reduced, the formation of a solidified layer can be suppressed; hence, the wall of the holding vessel is made smaller in the top and bottom portions than in the middle to thereby facilitate the discharge of the alloy from the holding vessel 30.

If the holding vessel 30 is made of a material having a thermal conductivity of less than 1.0 kcal/mh°C, the cooling time is prolonged to a practically undesirable level; hence, the holding vessel 30 should have a thermal conductivity of at least 1.0 kcal/mh°C. If the holding vessel 30 is made of a metal, its surface is preferably coated with a nonmetallic material (e.g. BN or graphite). the coating method may be either mechanical or chemical or physical. Both the magnesium and aluminum alloys are highly oxidizable metals, so if the holding vessel 30 is made of an air-permeable material or if the alloy is to be held for a long time in the vessel, the exterior to the vessel is preferably filled with a specified atmosphere (e.g. an inert or vacuum atmosphere). Even in the case of using the metallic vessel, the magnesium alloy which is highly oxidizable is desirably isolated by an inert or CO₂ atmosphere.

For preventing oxidation, an oxidation control element may be preliminarily added to the molten metal, as exemplified by Be and Ca in the case of the magnesium alloy and Be for the aluminum alloy. The shape of the vessel 30 is by no means limited to a tubular form and any other shapes that are suitable for the subsequent forming process may be adopted.

If the average rate of cooling in the holding vessel 30 is faster than 3.0 °C/s, it is not easy to permit the temperatures of various parts of the alloy to fall within the desired molding temperature range for establishment of the specified fraction liquid even if induction heating is employed and, in addition, it is difficult to generate spherical primary crystals. If, on the other hand, the average cooling rate is less than 0.014 °C/s, the cooling time is prolonged to cause inconvenience in commercial production. Therefore, the average rate of cooling in the holding vessel 30 should range preferably from 0.01 °C/s to 3.0 °C/s, more preferably from 0.05 °C/s to 1 °C/s.

Crystal nuclei can also be generated by pouring a refiner containing molten alloy directly into the holding vessel 30. In this case, if the poured alloy is superheated to more than 10°C above the liquidus temperature, fine spherical crystals cannot be produced no matter what cooling rate is adopted. Hence, the as-poured metal should be superheated to less than 10°C above the liquidus temperature. If the temperature of the alloy which is either liquid and superheated to less than 10°C above the liquidus temperature or partially solid, partially liquid alloy and less than 5°C below the liquidus temperature is allowed to decrease from the initial level and pass through a temperature zone 5°C below the liquidus temperature taking a time longer than 10 minutes, it is impossible to produce a fine spherical microstructure.

To avoid this problem, the temperature of the alloy is allowed to decrease from the initial level and pass through the temperature zone 5°C below the liquidus temperature within 10 minutes, preferably within 5 minutes, to thereby generate fine primary crystals in the solution of the alloy, which is taken out of the holding vessel 30, supplied into the forming mold 60 and shaped under pressure.

If enhanced cooling of the holding vessel 30 is necessary, either air or water or both are blown against the holding vessel 30 from its outside. Depending on the need, the cooling medium may be blown from at least two different, independently operable heights exterior to the holding vessel such that the blowing conditions and times can be varied freely. The cooling medium to be blown, the amount of blow, its velocity, speed, position and timing are variable with the alloy in the holding vessel 30, the material of which the vessel is made, its wall thickness, etc.

If the temperature of the yet to be shaped alloy in the holding vessel exceeds the limits of $\pm 5^{\circ}\text{C}$ of the desired molding temperature, a shaped part of uniform microstructure cannot be produced by casting. Hence, the temperature of the alloy in the holding vessel should be adjusted by induction heating to fall within the limits of $\pm 5^{\circ}\text{C}$ of the desired molding temperature.

5 If the vibrating rod 20 is to be used for the purpose of creating crystal nuclei in the alloy being poured into the holding vessel, it preferably satisfied the following two requirements: it should be coolable either internally or externally in order to provide for its continued use and generate many crystal; the surface of the vibrating rod 20 should be coated with a nonmetallic material. It should be noted that the use of rod that can be cooled internally but which is nonvibrating has the following disadvantage even if it is coated with a nonmetallic material: when the rod is pulled up from the poured
10 alloy, a solidified layer will stick extensively to the surface of the rod or many dendrites will form in the alloy in the holding vessel. To avoid this problem, the coolable rod must be vibrated when it is placed in contact with the molten metal.

The use of the vibrating rod 20 is effective in generating fine primary crystals in the alloy in the holding vessel but, at the same time, dendrites may occasionally form in those parts of the alloy which contact the inner surface of the holding vessel 30. To avoid this problem, the holding vessel 30 is preferably vibrated during pouring of the metal.

15 Table 1 sets forth the conditions for the preparation of semisolid metal samples to be shaped, and Table 2 sets forth the temperature distribution of yet to be shaped metal samples in the holding vessel, as well as the quality of shaped parts. As Fig. 3 shows, the forming step consisted of inserting the semisolid metal into the sleeve 50 and subsequent treatment with a squeeze casting machine. The forming conditions were as followed: pressure, 950 kgf/cm^2 ; injection rate, 0.5 m/s ; casting weight (inclusive of biscuits), 1.5 kg ; mold temperature, 230°C .
20

25

30

35

40

45

50

55

Table 1 (Continued on the next page)

Conditions for Preparation of Semisolid Metals to be Molded

Run No.	Alloy	Pouring temperature, °C	Nucleation	Temperature of metal in vessel, °C	Material of holding vessel	Molding temperature, °C	Average cooling rate, °C/s	Induction heating pattern		
								A	B	C
1	AC4CH	635	V	610	14	585	0.20			
2	AC4CH	635	V	609	14	585	0.10			
3	AC4CH	630	V	608	14	580	0.03			
4	AC4CH	625	Ti	610	14	585	0.15			
5	AC4CH	645	V	620	14	585	0.5			
6	AC4CH	635	V	610	14	585	0.18			
7	AC4CH	630	Ti	611	14	585	0.15			
8	AC4CH	640	V, Ti	610	14	582	0.13			
9	AZ91	615	V	590	14	575	0.13			
10	AZ91, Si, Sr	615	V	592	14	570	1.0			
11	AZ91, Ca	625	V	596	14	570	0.5			
12	AC7A	645	V	628	14	610	0.20			
13	AC4CH	635	Ti	610	14	580	0.25			
14	AC4CH	635	V	609	14	585	0.25			
15	AC4CH	635	V	610	0.3	585	0.08			
16	AC4CH	635	V	610	14	585	0.15			
17	AC4CH	635	Ti	610	14	585	4.0			
18	AC4CH	690	V	660	14	585	0.15			
19	AC4CH	635	Ti	610	14	580	0.25			

Notes:

(a. p.) AC4CH Al-7%Si-0.3%Mg-0.15%Ti 615°C

AZ91 Mg-9%Al-0.7%Mn-0.2%Na 595°C

AC7A Al-5%Mg-0.4%Na 635°C

(nucleation) V: based on claim 8; frequency 100 Hz; amplitude 0.1 mm per side

Ti: based on claim 9; 0.175% Ti and 0.005% B after addition of refiners

(induction heating)

pattern A: heated (-5 to +5°C) after the representative temperature reached the desired molding temperature.

pattern B: heated each time the decreasing representative temperature reached a specified level.

pattern C: heating started at a temperature at least 10°C below the desired molding temperature.

(material of holding vessel) Designated in terms of the thermal conductivity (kcal/mh°C) at 500°C: 14 for stainless steel SI; 18 for cast iron S2; 0.3 for ceramic C.

(heat-retained) Vessel was covered with a ceramic material having a thermal conductivity of 0.3 kcal/mh°C.

(heated) Heated with ir heater.

(blowing of cooling air or water) Air: blown from the outside of coil to cool vessel within the coil.

Water: blown against the vessel before it was placed within the coil.

(holding time) Holding time from the end of metal pouring into vessel until the start of shaping.

(degree of spheroidization of primary crystals) O, mostly spherical particles

Δ, coarse spherical particles

x, many dendrites and amorphous particles

Table 1 (Continued)

Conditions for Preparation of Semisolid Metals to be Shaped

Run No.	Alloy	Frequency		Temperature control of holding vessel		Cooling medium to be blown against holding vessel		Holding time, min	Metal weight, kg
		Before adjustment to molding temperature	After adjustment	Temperature control of holding vessel		Air or water	Temperature, °C		
				Top	Bottom				
1	AC4CH	8	8	heat-retained	-	Air	25	3.0	1.5
2	AC4CH	8	8	heat-retained	heat-retained	Air	200	5.5	15.0
3	AC4CH	8	8	heat-retained	-	-	-	40.0	15.0
4	AC4CH	8	8	heat-retained	heat-retained	-	-	4.3	1.5
5	AC4CH	8	8	heat-retained	-	Air	25	2.0	1.5
6	AC4CH	8	8	heat-retained	-	Water	25	3.0	1.5
7	AC4CH	8	45	heat-retained	heat-retained	Air	25	30.0	1.5
8	AC4CH	8	8	heat-retained	heated	Air	100	4.5	15.0
9	AZ91	8	8	heat-retained	heat-retained	-	-	3.0	0.9
10	AZ91, Si, Sr	8	8	heat-retained	heat-retained	Air	25	1.1	0.9
11	AZ91, Ca	8	8	heat-retained	heat-retained	Air	25	2.0	0.9
12	AC7A	8	8	heat-retained	heat-retained	Air	25	3.0	1.5
13	AC4CH	8	8	heat-retained	-	Air	25	3.0	1.5
14	AC4CH	8	8	heat-retained	heat-retained	Air	25	3.1	1.5
15	AC4CH	8	8	heat-retained	-	-	-	65.0	20.5
16	AC4CH	8	8	heat-retained	heat-retained	-	-	40.0	1.5
17	AC4CH	8	8	heat-retained	heat-retained	Water	25	0.3	1.5
18	AC4CH	8	8	heat-retained	heat-retained	-	-	10.0	1.5
19	AC4CH	8	8	heat-retained	-	Air	25	2.8	1.5

Table 2

Temperature of Semisolid Metals and Microstructure of Shaped Parts			
No.	Temperature distribution of yet to be shaped metal	Degree of spheroidization	Remarks
1	+2, -1	○	
2	+2, -1	○	
3	+2, -1	○	
4	+2, -1	○	
5	+3, -2	○	
6	+1, -2	○	
7	+2, -1	○	
8	+1, -1	○	Top and bottom portions of the vessel were about two thirds in thickness of the middle portion.
9	+1, -1	○	
10	+3, -4	○	
11	+2, -2	○	
12	+2, -1	○	
13	+2, -2	○	Extrusion molded
14	-10, 5	○	Induction heating started as at a temperature at least 10°C below the desired molding temperature.
15	-4, 5	△	Cooling rate too slow.
16	-2, -2	○	Held by induction heating for an unduly long time.
17	-4, 7	X	Cooling rate too fast.
18	-3, -5	X	Pouring temperature too high.
19	-7, 3	X	Vessel heat-retained insufficiently.

It should be noted that the data for Run No. 13 in Tables 1 and 2 refer to the conditions for forming with an extruding machine and the quality of the shaped part. The forming step consisted of inserting the semisolid metal into the container and extruding the same. The extruding conditions were as follow: extruding machine, 800 t; extruding rate (output rate), 80 m/min; extrusion ratio, 20; billet diameter, 75 mm.

In Run No. 14 (comparison) in Tables 1 and 2, the representative temperature of the alloy cooling in the holding vessel 30 had dropped to at least 10°C below the desired molding temperature before induction heating started and, hence, the temperature of the alloy could not be adjusted to fall within the limits of $\pm 5^\circ\text{C}$ of the desired molding temperature, thus making it impossible to produce a shaped part having a homogeneous microstructure.

In Run 15 (comparison), the cooling rate was slow and caused no big problems in temperature distribution but, on the other hand, the size of primary crystals exceeded 200 μm and the slow cooling was inconvenience to continuous production.

In Run No. 16 (comparison), the alloy in the holding vessel which had the temperatures of various parts adjusted to fall within the desired molding temperature range was continuously held as such by induction heating for an unduly long time and without changing the frequency; as a result, a liquid phase occurred extensively in the top peripheral portion of the semisolid metal.

In Run No. 17 (comparison), the cooling rate was so fast that even when induction heating was performed, the temperature of the alloy could not be adjusted to fall within the limits of $\pm 5^\circ\text{C}$ of the desired molding temperature range and no shaped part having a homogeneous microstructure could be produced; what is more, a solidified layer formed within the vessel, making it difficult to recover the semisolid metal from the vessel.

In Run No. 18 (comparison), the high pouring temperature led to an unduly hot melt in the vessel and, hence, there

were no residual crystal nuclei and many amorphous dendrites formed.

In Run No. 19 (comparison), the holding vessel was heat-retained only insufficiently so that the metal in the top of the vessel cooled prematurely, making it very difficult to recover the metal from the vessel.

In Run Nos. 1 - 13 according to the invention, there were obtained shaped parts having a homogeneous micro-structure which, as shown in Fig. 7, had no recognizable amorphous dendrites but comprised fine spherical primary crystals.

Fig. 14 is a graph showing how the B content and the degree of superheating of a melt during pouring affect the size and morphology of the primary crystals of AC4CH alloy (Al-7% Si-0.3% Mg-0.15% Ti). Unlike in the case of combined addition of Ti and B, no spherical crystals can be obtained at temperatures more than 30°C above the liquidus temperature when only Ti was added as a refiner.

Fig. 15 is a graph showing how the B content and the degree of superheating of a melt during pouring affect the size and morphology of the primary crystals of 7075 alloy (Al-5.5% Zn-2.5% Mg-1.6% Cu-0.15% Ti). The 7075 alloy was in contrast with the AC4CH alloy in that fine spherical crystals are obtained with high degree of superheating even when only Ti is used as a refiner.

Table 3 (Continued on the next page)

Run No.	Alloy	Degree of Superheating, °C	Refiner, %	Temperature of metal in vessel, °C	Passing time, min	Overall holding time, min	Method adding refiner	Material of ladle	Medium for cooling holding vessel	Induction heating
Invention	1 AC4CH+Ti	10	0.15	612	0.3	3.6	a	Cer.	-	Yes
	2 AC4CH+Ti, B	35	0.15	613	0.5	3.9	c	Cer.	-	Yes
	3 AC4CH+Ti, B	45	0.15	616	1.0	5.0	a	Cer.	-	Yes
	4 AC4CH+Ti, B	30	0.15	614	0.6	4.0	d	Iron	-	Yes
	5 AC4CH+Ti, B	30	0.15	613	0.3	3.0	b	Cer.	Air	Yes
	6 AC4CH+Ti, B	30	0.15	617	6.0	25.0	a	Cer.	Water	Yes
	7 AZ91+Ca	15	0.15	591	0.3	3.1	a	Iron	-	Yes
	8 AZ91+Si, Sn	15	0.4	595	0.3	3.2	a	Iron	-	Yes
	9 7075	35	0.05	633	1.5	3.8	a	Cer.	-	Yes
	10 7075	47	0.15	636	1.6	3.0	a	Cer.	-	No
Comparison	11 7075	15	0.03	635	1.4	2.7	a	Iron	-	No
	12 7075	15	0.03	633	1.5	2.9	a	Iron	-	No
	13 AC4CH+Ti	35	0.15	614	0.5	4.0	a	Cer.	-	Yes
	14 AC4CH+Ti, B	60	0.15	613	1.2	3.9	c	Cer.	-	Yes
	15 AC4CH+Ti, B	35	0.15	615	14.5	25.5	a	Cer.	-	Yes
	16 AC4CH+Ti, B	30	0.15	616	0.5	40.0	a	Cer.	-	Yes
	17 AC4CH+Ti, B	30	0.15	613	0.5	2.5	a	Cer.	Air	Yes
	18 AC4CH+Ti, B	30	0.15	614	0.5	25.0	a	Cer.	Air	No
	19 AC4CH	15	-	613	0.3	3.7	a	Cer.	-	Yes
	20 AZ91	15	-	592	0.2	3.00	a	Iron	-	Yes
	21 AZ91+Sr	15	0.015	593	0.2	31.0	a	Iron	-	Yes
	22 7075	30	-	634	1.5	2.7	a	Cer.	-	Yes

Alloy AC4CH Al-7%Si-0.3%Mg (Ti not added)

AZ91 Mg-9%Al-0.7%Zn-0.4%Mn

7075 Al-5.5%Zn-2.5%Mg-1.6%Cu (Ti not added)

Temperature of metal in vessel: Temperature of as-poured metal

Passing time:

Time required for the as-poured melt to decrease in temperature from the initial level and through temperature zone 5°C below the liquidus temperature.

Overall holding time:

Holding time required for the temperature of the as-poured melt to decrease from the initial level to the molding temperature.

Method of adding refiner: a, melted in holding furnace;

b, melted in ladle;

c, diluted;

m.p.: AC4CH 615°C

AZ91 595°C

7075 635°C

Material of ladle:

Cer.: Ceramics;

Iron: Stainless steel or cast iron

Heating or heat retention of holding vessel: both top and bottom portions of vessel were heated or heat-retained.

Fraction liquid:

Estimated from equilibrium phase diagram and cooling curve.

Metal temperature distribution:

○, within 15°C of the desired temperature.

x, outside 15°C of the desired temperature.

Table 3 (Continued)

Run No.	Alloy	Heating or heat-retention of holding vessel	Fraction liquid before shaping, %	Temperature distribution of metal in holding vessel	Amount of spherical particles	Size of primary crystals μm	Remarks
1	AC4CH+Ti	Yes	60	○	○	100	
2	AC4CH+Ti, B	Yes	60	○	○	100	
3	AC4CH+Ti, B	Yes	60	○	○	115	
4	AC4CH+Ti, B	Yes	60	○	○	95	
5	AC4CH+Ti, B	Yes	60	○	○	95	
6	AC4CH+Ti, B	Yes	60	○	○	130	
7	AZ91+Ca	Yes	60	○	○	140	
8	AZ91+Si, Sn	Yes	60	○	○	110	
9	7075	Yes	60	○	○	105	
10	7075	Yes	60	○	○	80	
11		Yes	60	○	○	90	
12		Yes	60	○	○	90	
13	AC4CH+Ti	Yes	60	○	×	150	Degree of superheating too high
14	AC4CH+Ti, B	Yes	60	○	×	100	Degree of superheating too high
15	AC4CH+Ti, B	Yes	60	○	×	150	Passing time too long
16	AC4CH+Ti, B	Yes	60	○	×	180	Holding time too long
17	AC4CH+Ti, B	No	60	×	○	100	Uneven distribution of metal temperature
18	AC4CH+Ti, B	No	60	×	○	110	Uneven distribution of metal temperature
19	AC4CH	Yes	60	○	×	180	Refiner absent
20	AZ91	No	60	○	×	200	Refiner absent
21	AZ91+Sr	Yes	60	○	×	160	Only Sr added
22	7075	Yes	60	○	×	170	Refiner absent

Table 3 sets forth the conditions for the preparation of semisolid metal samples and the results of examination of the microstructure of shaped parts. As Fig. 13 shows, the forming step consisted of inserting the semisolid metal into

the injection sleeve 170 and subsequent treatment with a squeeze casting machine. The forming conditions were as follows: pressure, 950 kg/cm²; injection rate, 0.5 m/s; casting weight (inclusive of biscuits), 1.5 kg; mold temperature, 230°C.

In Run Nos. 13 and 14 (comparisons) in Table 3, the degree of superheating above the liquidus temperature was so high that no fine spherical crystals were obtained but only coarse primary crystals formed (see Fig. 19).

In Run No. 15 (comparison), the temperature of the melt poured into the holding vessel 30 was allowed to decrease from the initial level and pass through a temperature zone 5°C below the liquidus temperature taking a time longer than 10 minutes. In Run No. 16 (comparison), the holding time was unduly long. Hence, only coarse primary particles were obtained in these runs.

In Run Nos. 17 and 18, neither top nor bottom portion of the holding vessel 30 was heat-retained or heated, so even when induction heating was effected, the alloy in the holding vessel 30 had an uneven temperature distribution.

In Run Nos. 19 and 20, the alloy samples produced only coarse primary crystals since they did not contain a refiner. See Fig. 20.

In Run No. 21 (comparison), only Sr was added as a refiner and the shaped part was not much refined compared to that of the alloy containing no Sr. See Fig. 21 for the microstructure of the shaped part obtained in Run No. 21.

In Run No. 22, the alloy sample did not contain a refiner and the degree of its superheating above liquidus temperature was unduly high; hence, only coarse primary crystals formed as shown in Fig. 22.

In contrast, the alloy samples prepared in Run Nos. 1 - 12 according to the fine spherical primary particles as shown in Figs. 16, 17 and 18.

As will be understood from the foregoing description, according to the method of the invention for shaping semisolid metals, shaped parts having fine and spherical microstructures can be produced in a convenient, easy and inexpensive manner without relying upon agitation by the conventional mechanical and electromagnetic methods.

Claims

1. A method of shaping a semisolid metal, in which liquid alloy having crystal nuclei and being at a temperature not lower than the liquidus temperature or a partially solid, partially liquid alloy having crystal nuclei and being at a temperature less than the liquidus temperature but not lower than the molding temperature is poured into a holding vessel having a thermal conductivity of at least 1 kcal/mh°C, cooled at an average cooling rate of 0.01 °C/s - 3.0 °C/s and held as such until just prior to the start of shaping under pressure, whereby fine primary crystals are generated in said alloy solution and the alloy within said holding vessel is temperature adjusted by induction heating such that the temperatures of the various parts of the alloy fall within the desired molding temperature range for the establishment of a specified liquid fraction not later than the start of shaping and the alloy is recovered from said holding vessel, supplied into a forming mold and shaped under pressure.
2. The method according to claim 1, wherein the induction heating is for effecting thermal adjustment such that a specified amount of electric current is applied for a specified time immediately after the pouring of the molten alloy before the representative temperature of the alloy slowly cooling in the holding vessel has dropped to at least 10°C below the desired molding temperature, so that the temperatures of the various parts of the alloy within said holding vessel fall within the limits of ±5°C of the desired molding temperature.
3. The method according to claim 1 or 2, wherein once the temperatures of the various parts of the alloy within the holding vessel have been adjusted by induction heating to fall within the desired molding temperature range within a specified time, the temperature of said alloy is held until just before the start of the shaping step by induction heating at a frequency comparable to or higher than the frequency used in the induction heating for the preceding temperature adjustment.
4. The method according to any one of claims 1-3, wherein either the top portion or the bottom portion or both of the holding vessel are heat-retained or heated to a higher temperature than the middle portion or the top and bottom portions of the holding vessel are smaller in wall thickness than the middle portion.
5. The method according to any one of claims 1-4, wherein the alloy within the holding vessel is cooled by blowing either air or water or both against said holding vessel from its outside.
6. The method according to claim 5, wherein either air or water or both which are at a specified temperature are blown from at least two different, independently operable heights exterior to the holding vessel such that the blowing conditions and times can be varied freely.

7. The method according to any one of claims 1-6, wherein the alloy to be supplied into the forming mold has a liquid fraction of at least 1.0% but less than 75%.
- 5 8. The method according to any one of claims 1-7, wherein the crystal nuclei are generated by vibrating the alloy which builds up in the holding vessel by pouring in a melt superheated to less than 50°C above the liquidus temperature, the vibration being applied to said alloy either by means of a vibrating rod which is submerged in the melt during its pouring so that it has direct contact with the alloy or by vibrating not only the vibrating rod but also the holding vessel as the alloy is poured into said holding vessel.
- 10 9. The method according to any one of claims 1-8, wherein the crystal nuclei are generated by pouring a molten aluminum alloy into the holding vessel, said alloy being held superheated to less than 50°C above the liquidus temperature and containing 0.001% - 0.01% B and 0.005% - 0.3% Ti.
- 15 10. The method according to any one of claims 1-8, wherein the crystal nuclei are generated by pouring a molten magnesium alloy into the holding vessel, said alloy being held superheated to less than 50°C above the liquidus temperature and containing 0.01% - 1.5% Si and 0.005% - 0.1% Sr or 0.05% - 0.30% Ca alone.
- 20 11. A method of shaping a semisolid metal, in which a molten aluminum or magnesium alloy containing a crystal grain refiner which is held superheated to less than 50°C above the liquidus temperature is poured directly into a holding vessel without using any cooling jig and held for a period of from 30 seconds to 30 minutes as the melt is cooled to the molding temperature where a specified liquid fraction is established such that the temperature of the poured alloy which is liquid and superheated to less than 10°C above its liquidus temperature or which is partially solid, partially liquid and is less than 5°C below the liquidus temperature is allowed to decrease from the initial level and pass through a temperature zone 5°C below the liquidus temperature within 10 minutes, whereby fine primary crystals are generated in said alloy solution, and the alloy is recovered from the holding vessel, supplied into a forming mold and shaped under pressure.
- 25 12. The method according to claim 11, wherein the aluminum alloy has 0.03% - 0.30% Ti added and superheated to less than 30°C above the liquidus temperature as it is poured into the holding vessel.
- 30 13. The method according to claim 11, wherein the aluminum alloy has 0.005% - 0.30% Ti and 0.001% - 0.01% B added and superheated to less than 50°C above the liquidus temperature as it is poured into the holding vessel.
- 35 14. The method according to claim 11, wherein the temperature of the alloy poured into the holding vessel is held by temperature adjustment through induction heating such that the temperatures of the various parts of said alloy within said holding vessel are allowed to fall within the desired molding temperature range for the establishment of a specified liquid fraction not later than the start of shaping.

40

45

50

55

FIG. 1

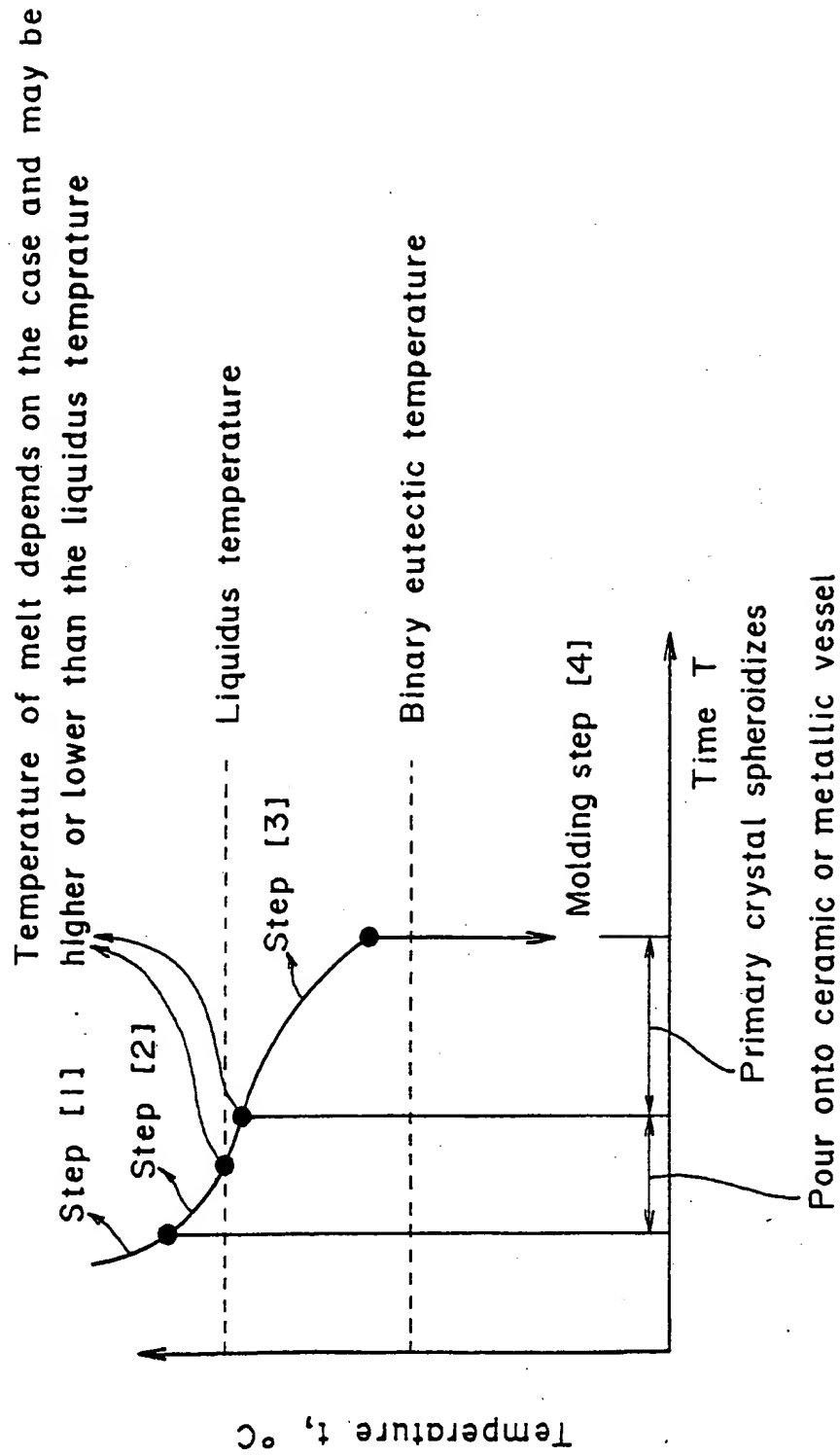


FIG. 2

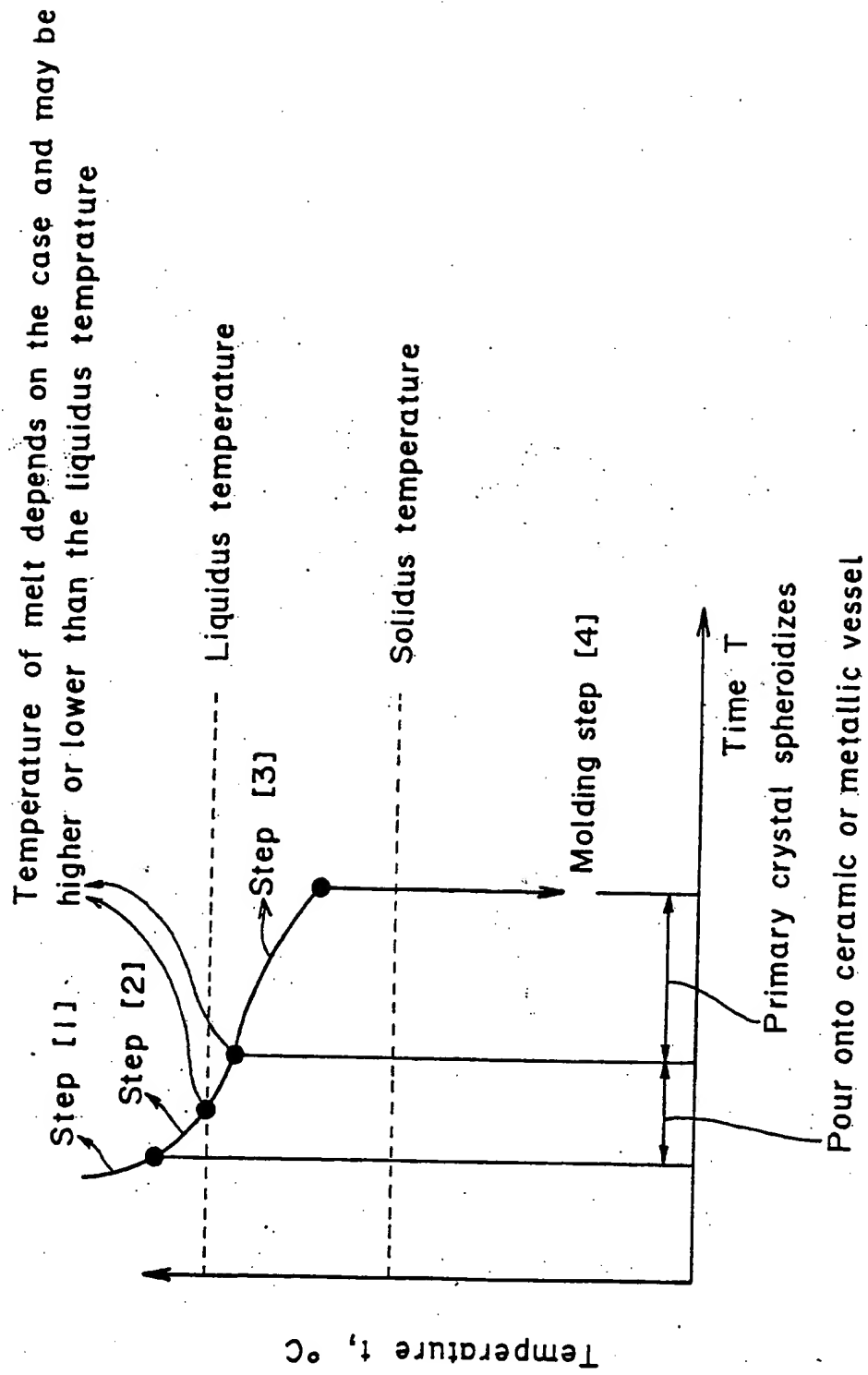


FIG. 3

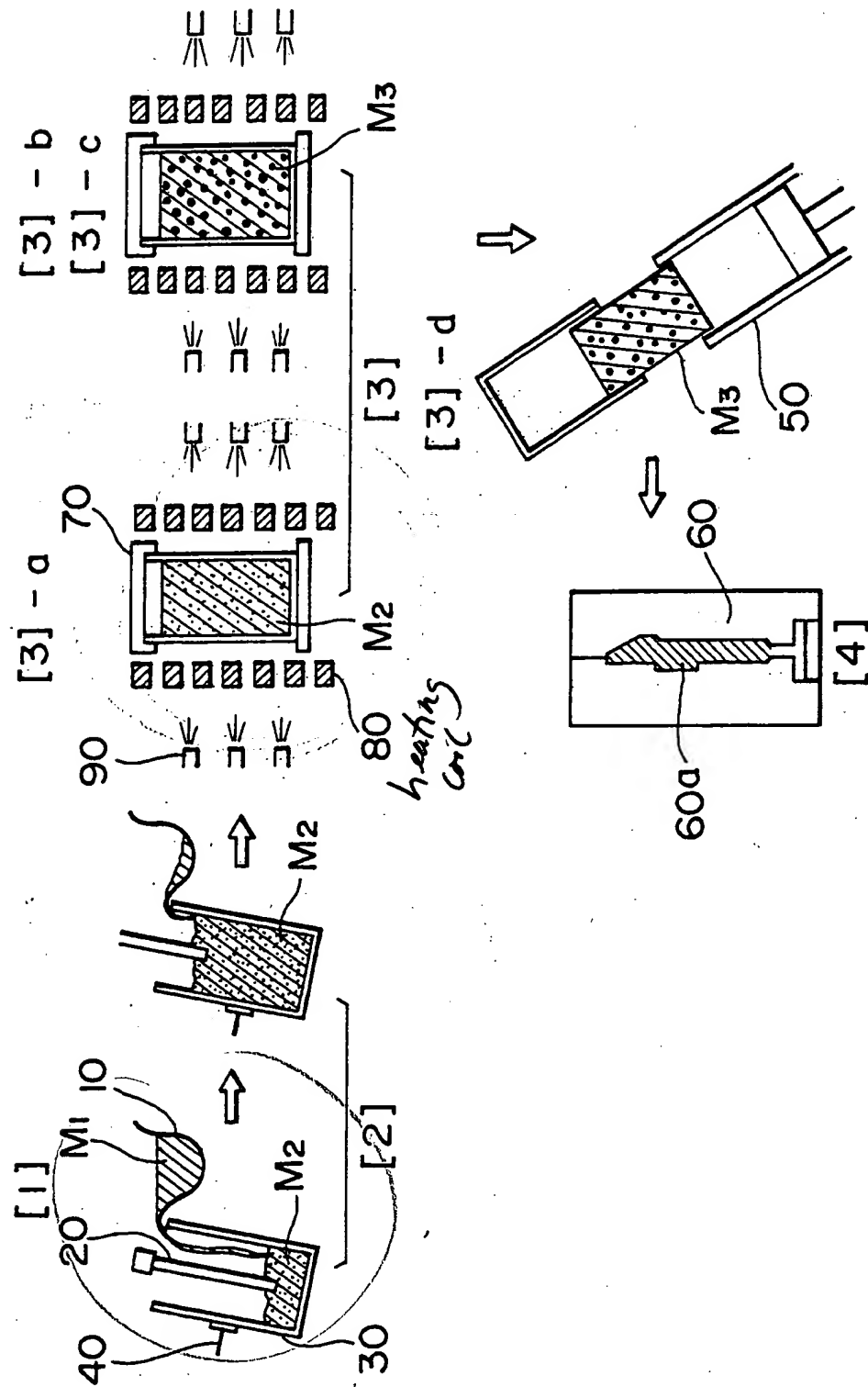


FIG. 4

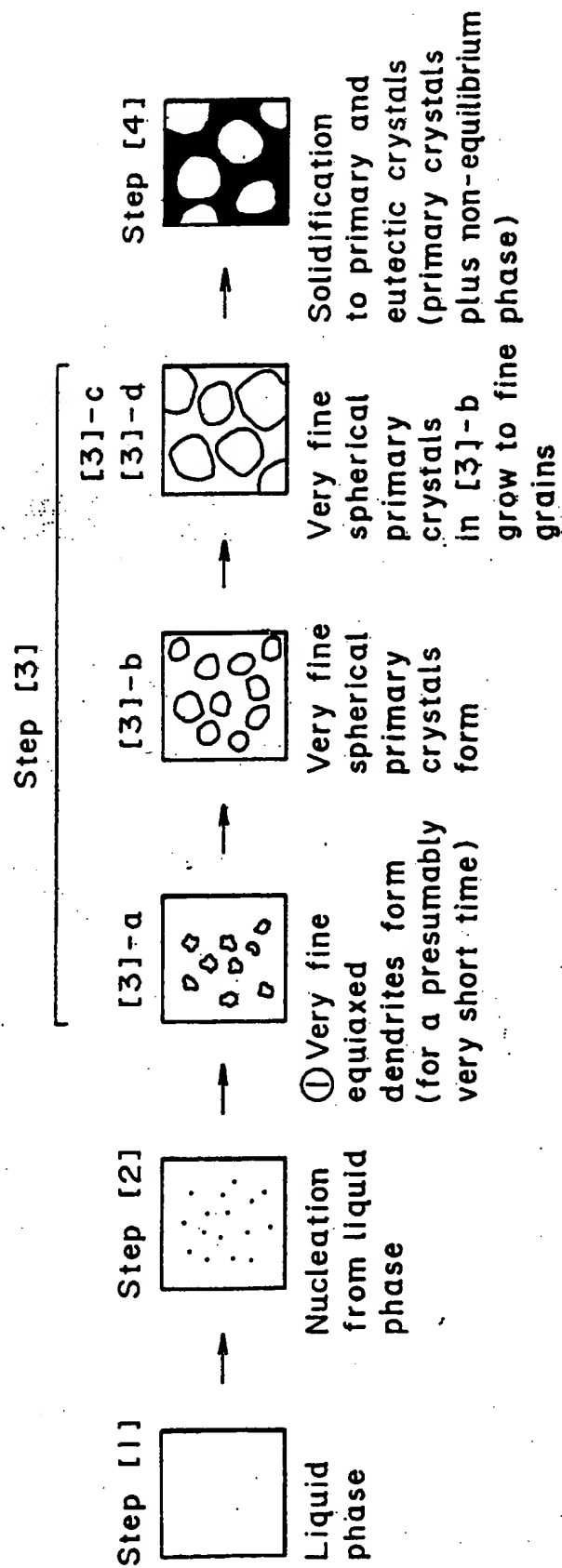


FIG. 5

Temperature of melt depends on the case and may be higher or lower than the liquidus temperature

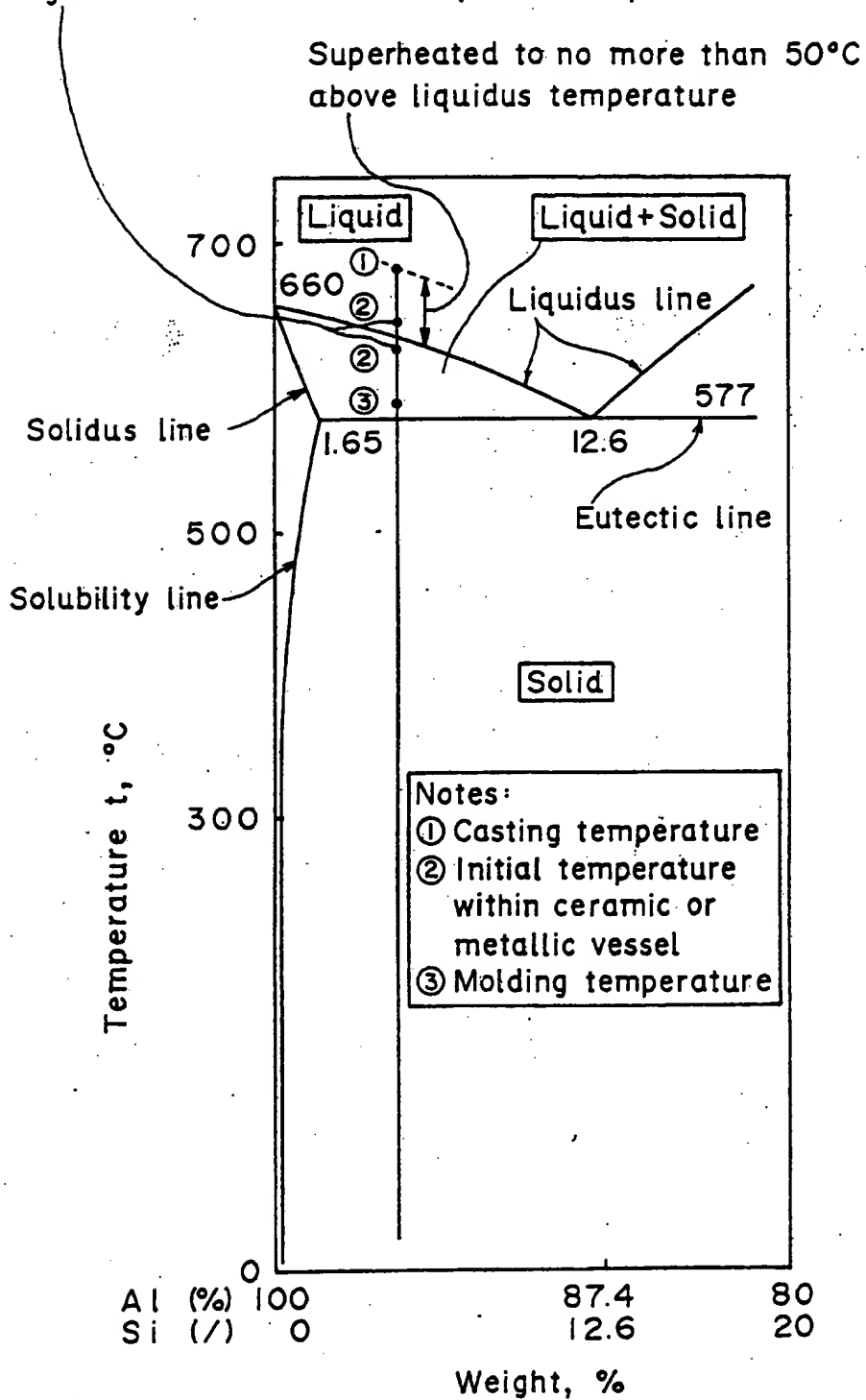


FIG. 6

Temperature of melt depends on the case and may be higher or lower than the liquidus temperature

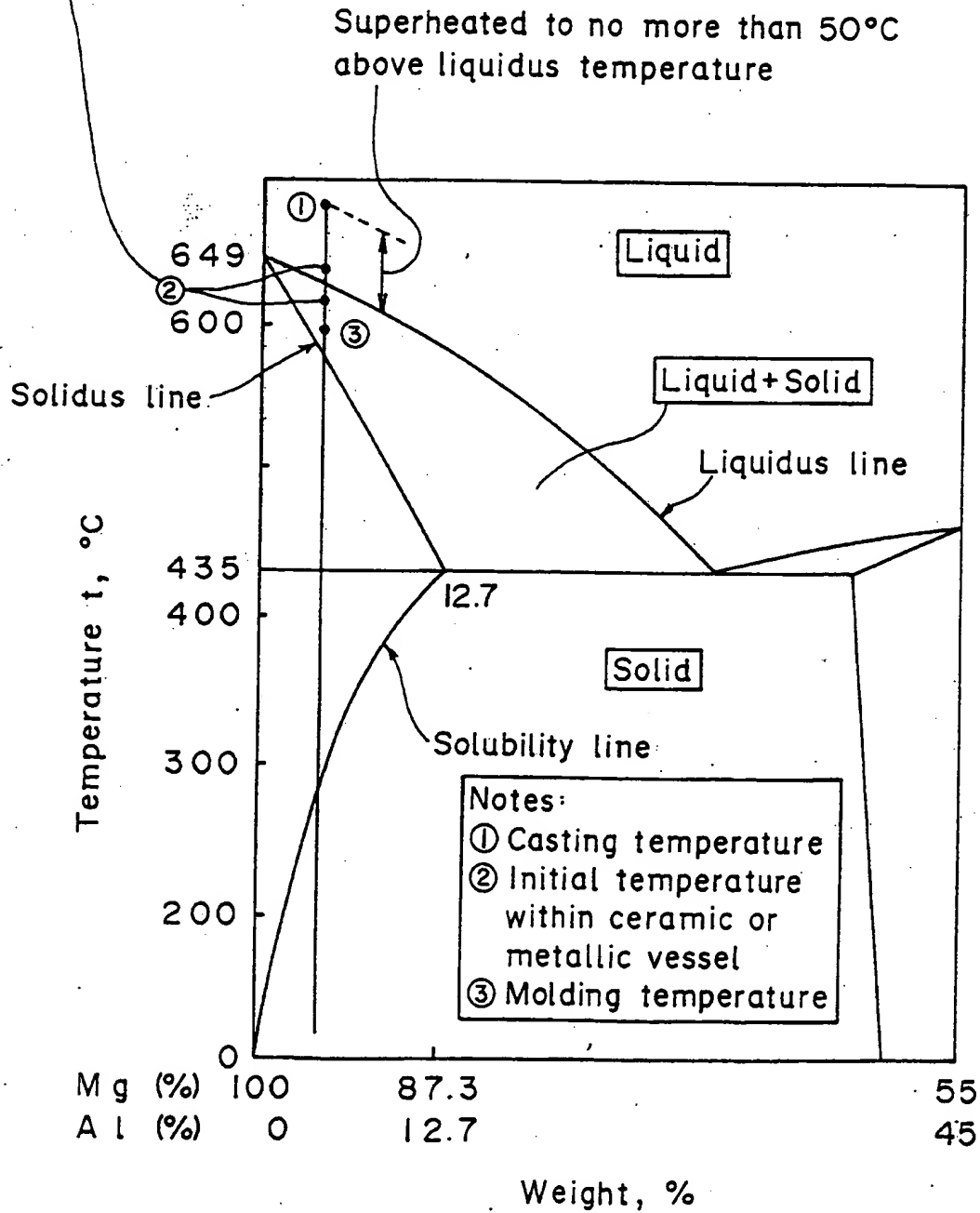


FIG. 7

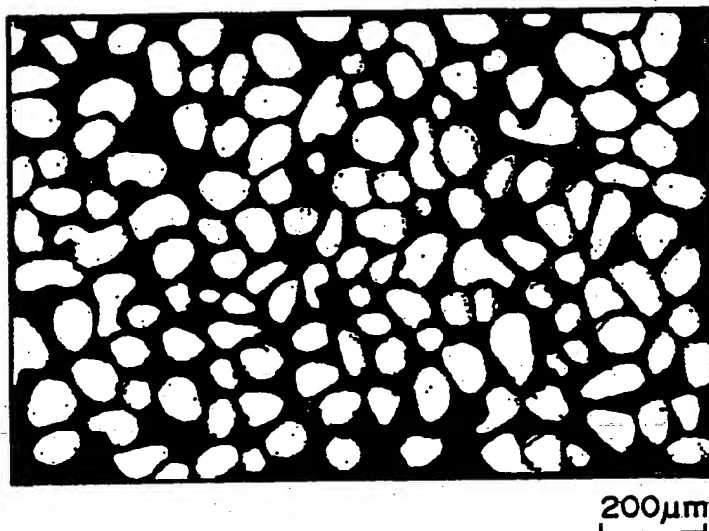


FIG. 8 Prior Art

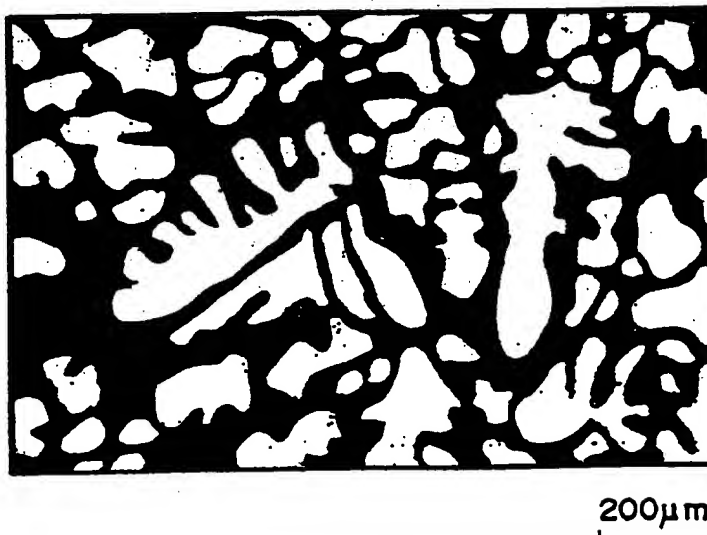


FIG. 9

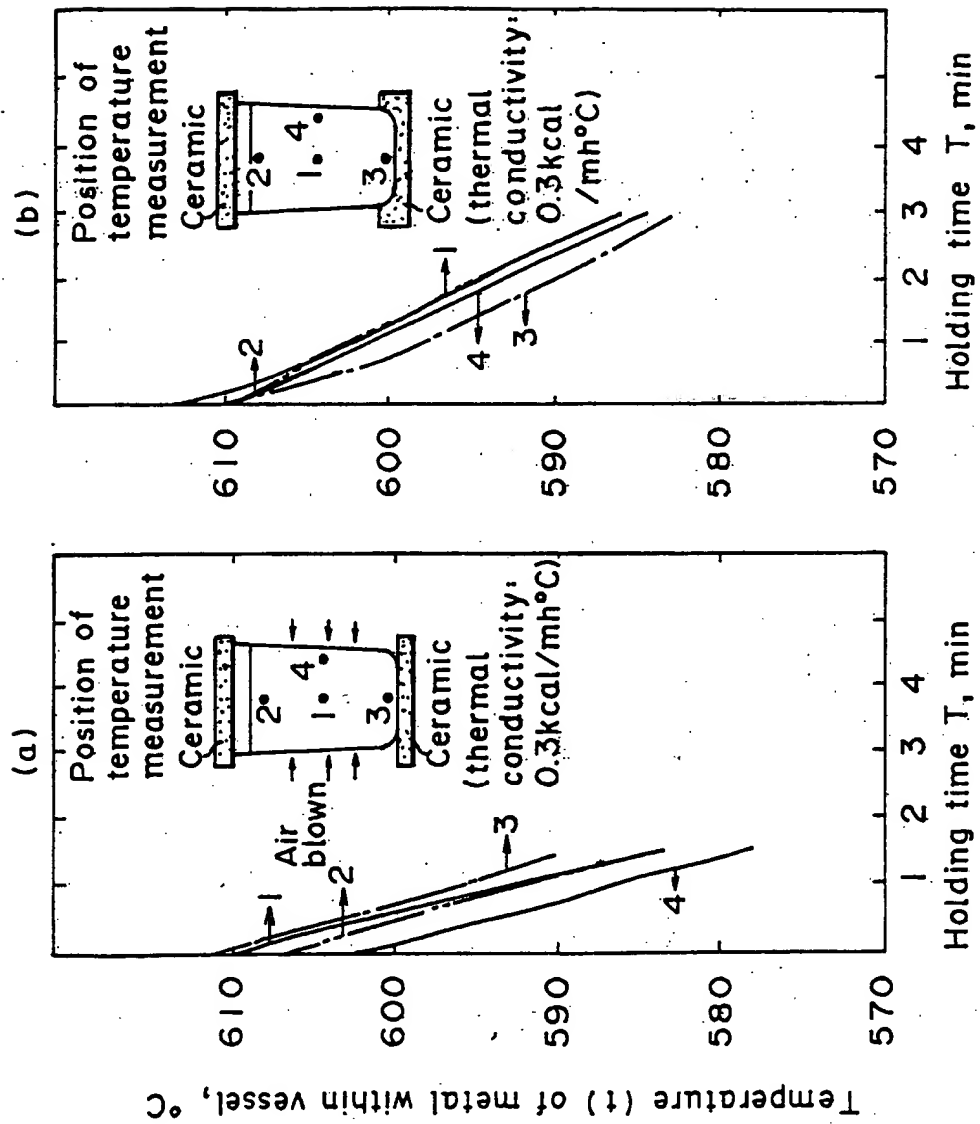
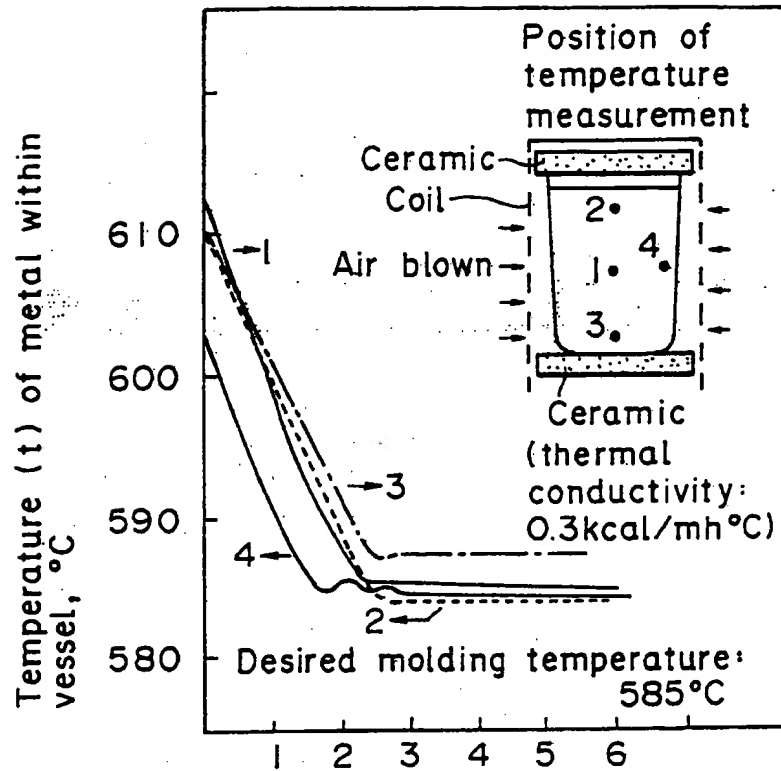
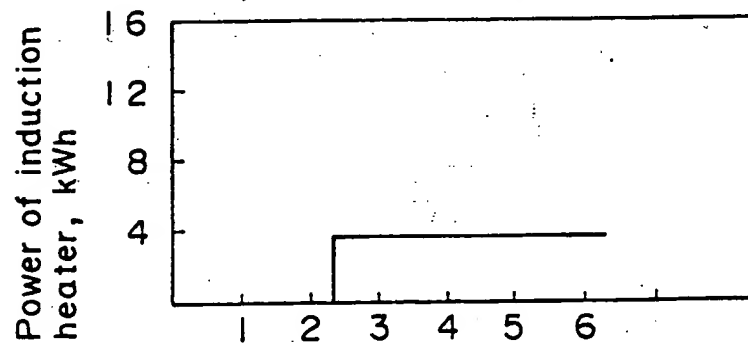


FIG. 10

(a)



(b)



(c)

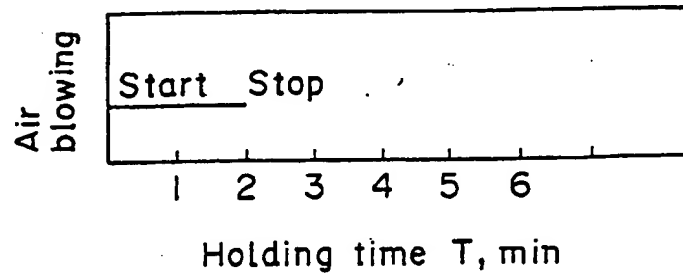


FIG. 11

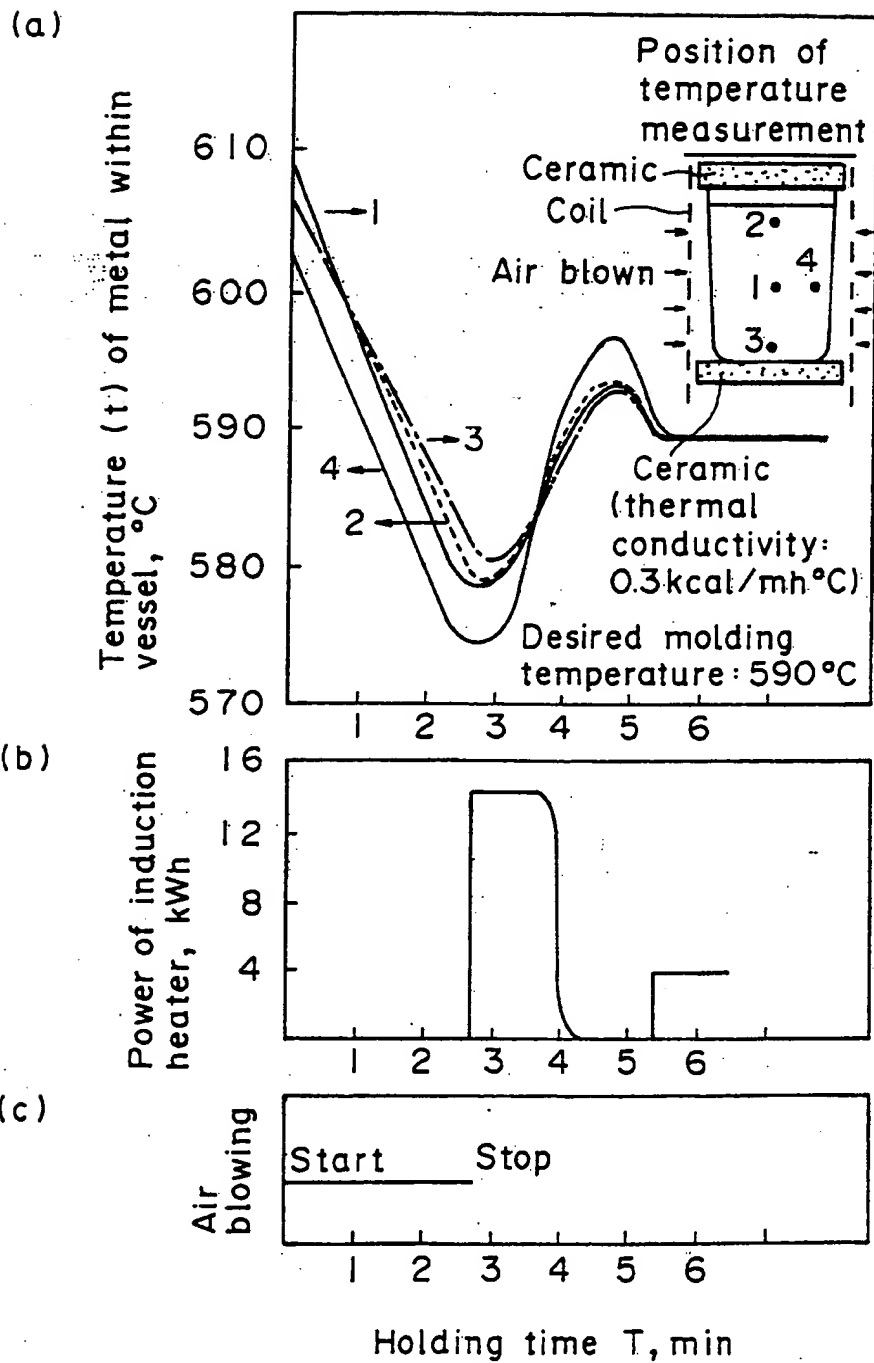
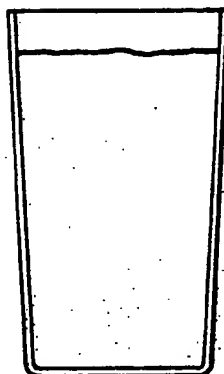
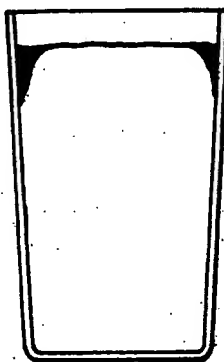


FIG. 12

(a) When molding temperature is reached



(b) When heated and held with rf induction heater (at 8 kHz) for 20 min after molding temperature was reached



(c) When heated and held with rf induction heater (at 40 kHz) for 20 min after molding temperature was reached

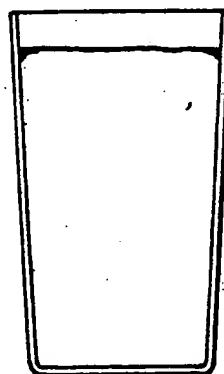


FIG. 13

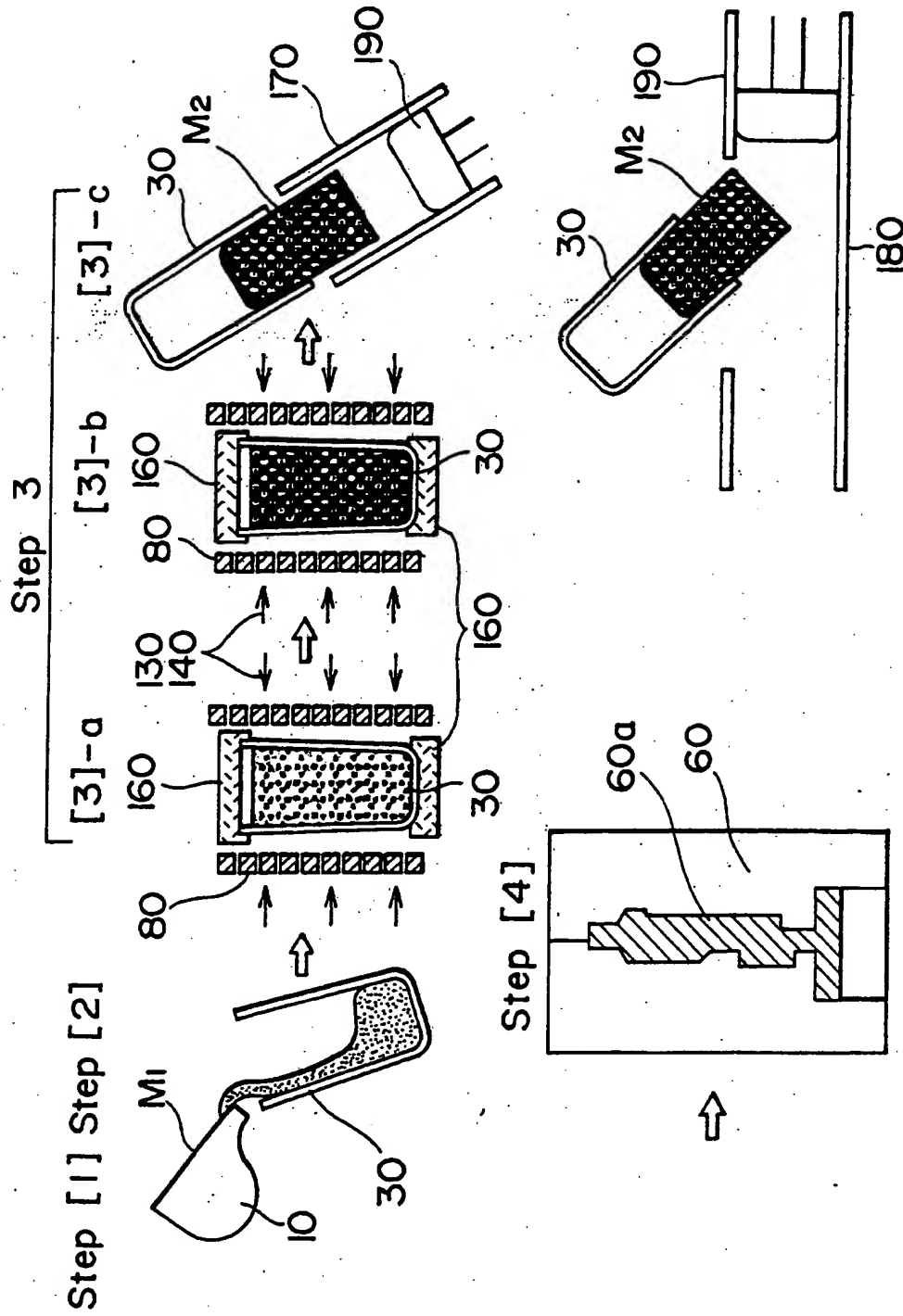


FIG. 14
AC4CH(Al-7Si-0.3Mg-0.15Ti)

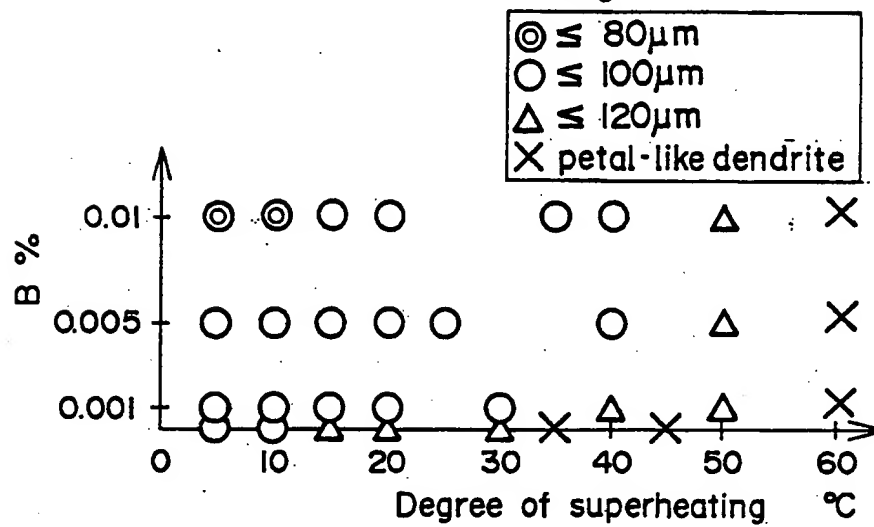


FIG. 15
7075(Al-5.5Zn-2.5Mg-1.6Cu-0.15Ti)

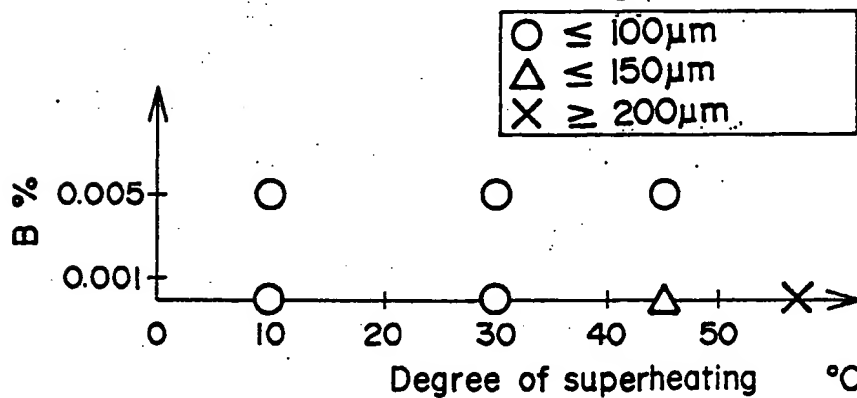


FIG. 16

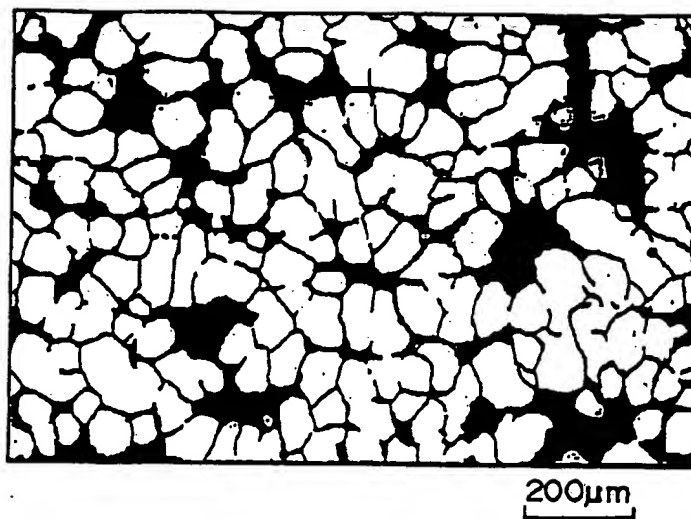


FIG. 17

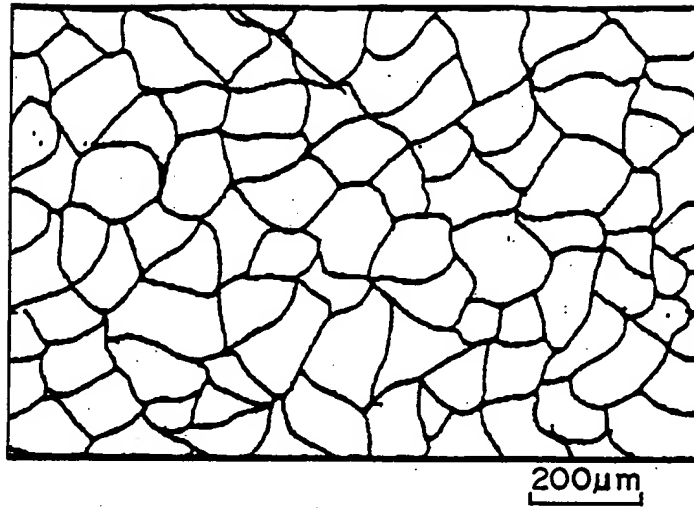


FIG. 18

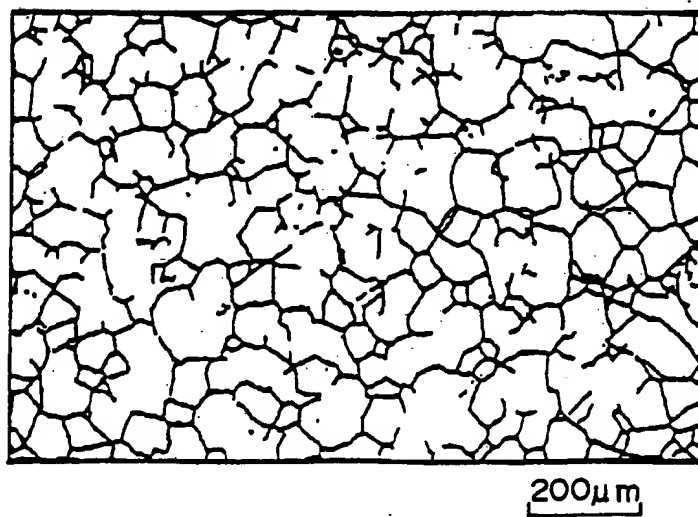


FIG. 19 Prior Art

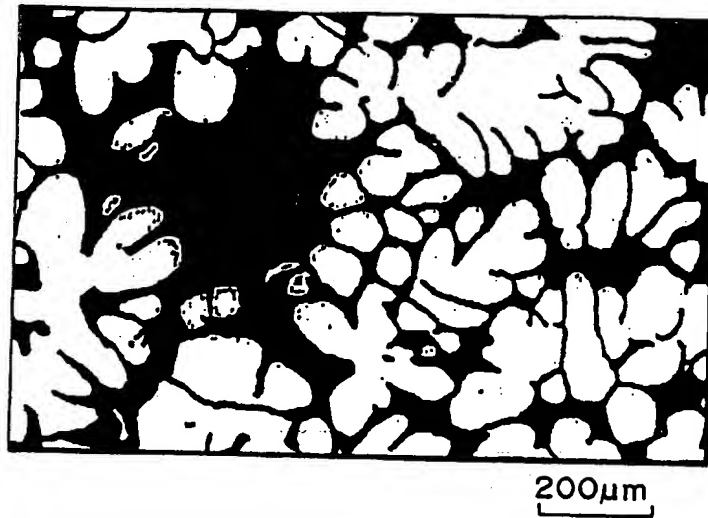


FIG. 20 Prior Art

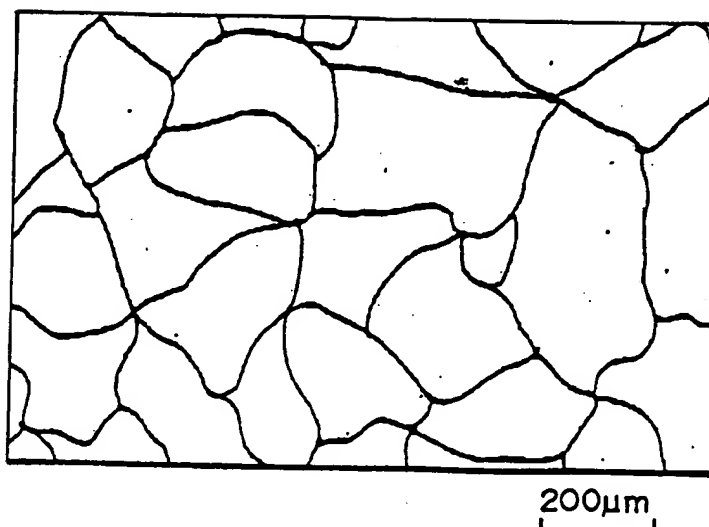


FIG. 21 Prior Art

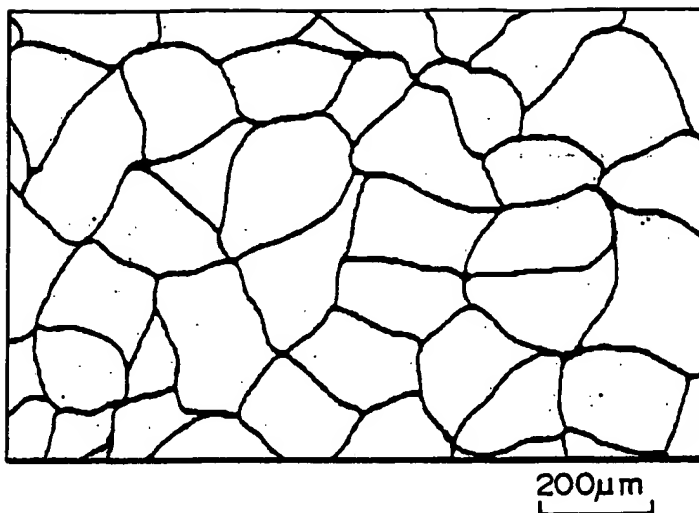
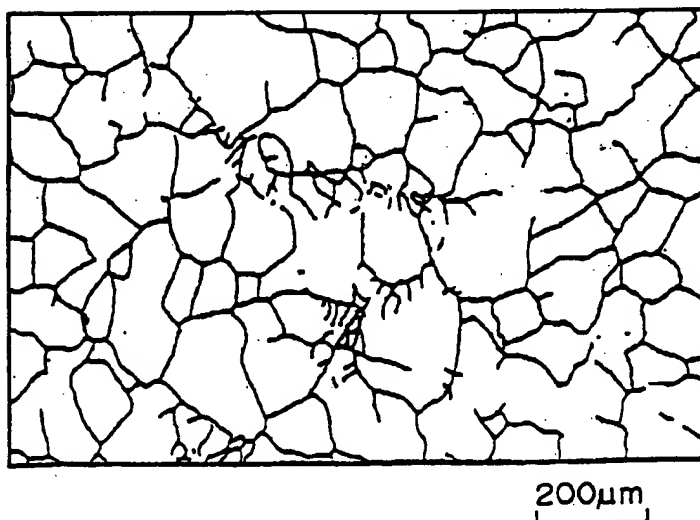


FIG. 22 Prior Art





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 11 9554

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P, X	EP 0 745 694 A (UBE INDUSTRIES) * page 8, line 28 - line 29; claims 1, 28 * * page 9, line 56 - page 10, line 11 * * page 17, line 39 - line 57 * ---	1-14	C22C1/00 B22D17/00
A	EP 0 701 002 A (UBE INDUSTRIES) * claim 1 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C22C B22D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 February 1998	Examiner Gregg, N
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503.03.92 (P4/C01)